A New Strategy for the Synthesis of Diverse Benzo[*a*]carbazoles *via* Divergent Catalytic Michael Reaction

Kripalaya Ratheesh Arya,[a] Hazel A. Sparkes,[b] Karnam Jayarampillai Rajendra Prasad*[a]

[a] Department of Chemistry, Bharathiar University, Coimbatore - 641046, India.

[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom.

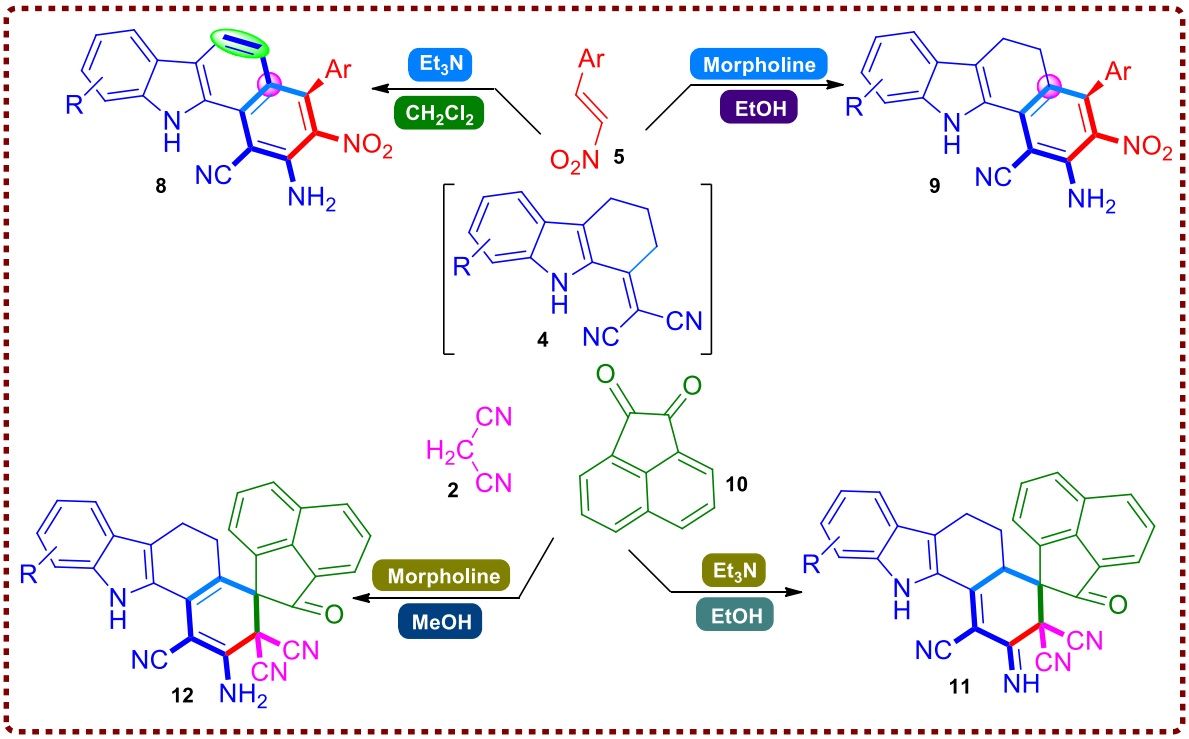
Abstract

A new type of divergent tandem Michael addition of α,α-dicyanomethylidenecarbazoles with β-nitrostyrenes, afforded multifunctional benzo[*a*]carbazoles [BCs] and benzodihydro[*a*]carbazoles [BDHCs] in good yields. In addition, the direct multicomponent transformation of α,α-dicyanomethylidenecarbazoles, acenaphthenequinone and malononitrile results in the formation of an unreported imino and amino functionalized spiro[acenaphthylene-8',4-benzo[*a*]carbazole] hybrids *via* amine-controlled divergent reactions. The spiro products also were obtained in good yields. The structures of the synthesized cycloadducts were confirmed by elemental analysis, spectral data (FT-IR, ^{1}H, ^{13}C NMR and HRMS) and by single crystal X-ray diffraction studies. The application of this divergent tandem Michael addition protocol is beneficial from the view point of diversity-oriented one-pot synthesis of benzo[*a*]carbazole derivatives from simple starting materials.

*Corresponding author e-mail: prasad_125@yahoo.com, Tel: +91-422-2423763, Fax: +91-422-2422387.

Introduction

The divergent catalytic processes furnish quick access to structurally diversified compounds from a common substrate *via* controlled reaction mechanism.[1,2] The tandem divergent catalysis [TDC] is amore promising, largely unexplored and yet challenging strategy, which combines the key advantages intrinsic to both tandem reactions[3] and divergent catalysis to provide different structures from a common reagent by avoiding the isolation of intermediates, thereby alleviating waste generation.[4] Although the benefits of tandem divergent catalytic processes are obvious, their development is still rare and challenging. In this regard, we focused on the reactivity of α,α-dicyanomethylidenecarbazoles in order to exploit controllable reaction pathways for divergent reactions (Scheme 1).

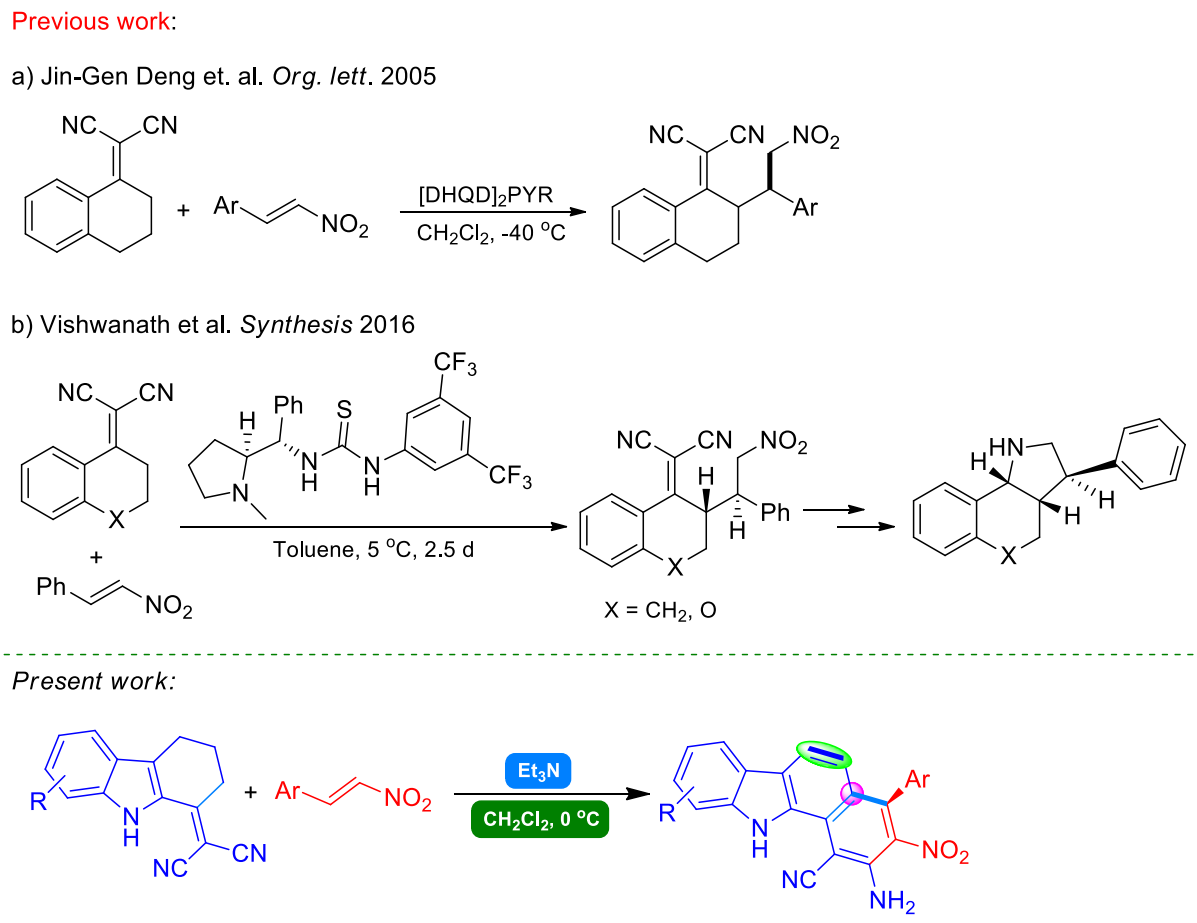


Scheme 1 Amine-controlled tandem synthesis of benzo[*a*]carbazoles from dicyanomethylidenecarbazoles.

α,α-Dicyanoalkenes have been exploited as vinylogous nucleophiles, Michael acceptors and dienophiles in a variety of organic reactions for the construction of multifunctional molecules. However, their potential as vinylogous donors in synthetic chemistry was recognized after the independent publications by Jørgensen, *et al.* in 2005.[5] The benzo[*a*]carbazoles [BCs], containing an aromatic ring fused to the *a*-face of the carbazole nucleus, are potential candidates for cancer treatment as a result of their DNA intercalative binding properties and planar

conformation.[6] Although these systems are found rarely in natural products, benzo[*a*]carbazole structural motifs display diverse biological activities such as antifungal, antitumor, anti-inflammatory, antiestrogenic and kinase inhibitory properties.[7-15]

Vinylogous Michael addition was involved as a key step in the synthesis of polysubstituted benzene derivatives in a one-pot tandem reaction.[16] Nitroolefins are promising candidates among many Michael acceptors because of their strong electron withdrawing nitro group which could be easily transformed into a wide variety of biologically active building blocks and products.[17-19] The literature survey reveals various reports on the synthesis of Michael adducts through asymmetric Michael addition of α,α-dicyanoalkenes to nitroolefins. Here we present for the first time the preparation of multifunctionalized benzo[*a*]carbazoles *via* direct vinylogous Michael addition of α,α-dicyanomethylidene carbazoles to nitrostyrenes (Scheme 2).



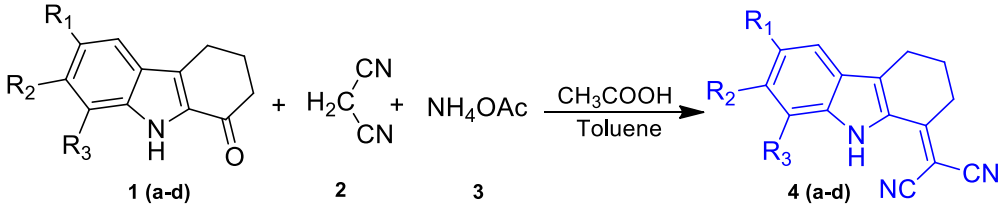
Scheme 2 Michael addition reaction involving dicyanoolefins and nitrostyrenes.

Spiro-acenaphthenequinone, especially when attached to other heterocycles, occupy an important position amongst the different families of spirocyclic compounds, as a result of their pharmaceutical properties.[20-22] The biological importance of benzo[*a*]carbazole and spiro-acenaphthenequinone in conjunction with our interest in the synthesis of novel hybrid spirocompounds, has led us to report the catalyst-controlled synthesis of novel imino and amino functionalized spiro[acenaphthylene-8',4-benzo[*a*]carbazole] derivatives *via* three component reaction of α,α-dicyanomethylidene carbazoles, malononitrile and acenaphthenequinone.

In light of these findings, we wish to report, herein, an amine-controlled divergent Michael addition methodology for the synthesis of both highly substituted benzo[*a*]carbazole and spiroacenaphthylene-benzo[*a*]carbazole derivatives having the potential to serve as templates for new biologically active molecules, from a common synthon under mild reaction conditions.

Results and discussion

The present study began with the synthesis of the precursor,1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** *via* condensation of 2,3,4,9-tetrahydrocarbazol-1-ones **1** with malononitrile **2** and ammonium acetate **3** in the presence of a catalytic quantity of acetic acid in toluene, according to the reported procedure[23] (Scheme 3).

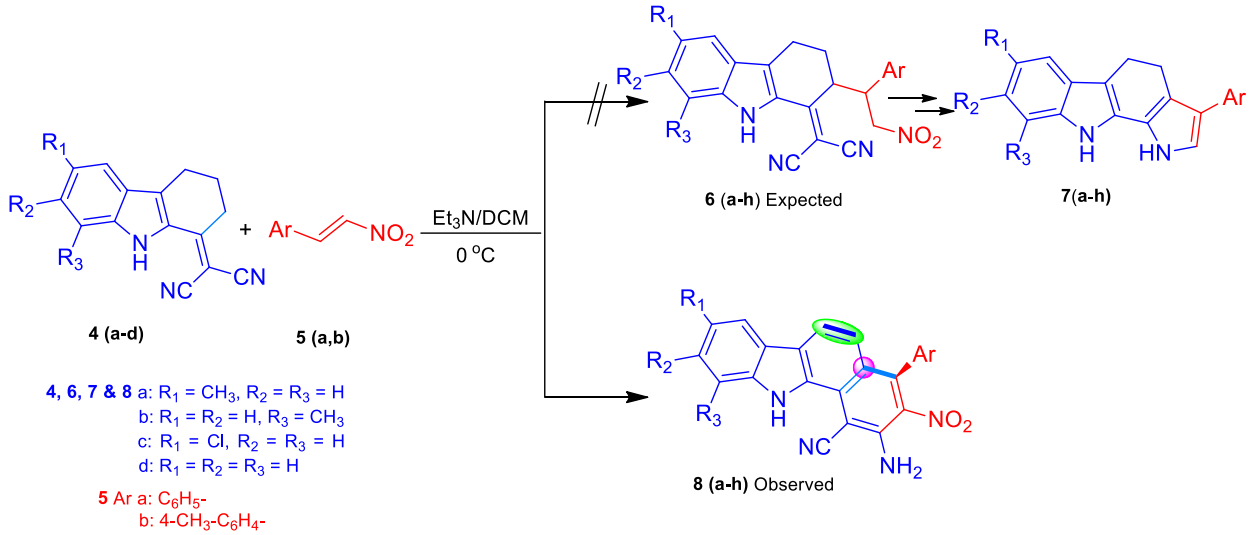


Scheme 3 Synthesis of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4**.

The vinylogous Michael addition reaction of α,α-dicyanoalkene with nitroolefine to obtain the Michael adduct has been known for long time.[24,25] However, they were not able to afford an annulated product. Recently, Vishwanath *et al*,[26] envisaged the possibility of forming cyclized products *via* Michael addition of vinyl malononitriles to nitrostyrenes using a multistep methodology (Scheme 2a,b).

Prompted by the encouraging literature precedent, we embarked on the synthesis of the Michael adducts **6** (**a**-**h**) which are suitable intermediates to derive the 3-aryl-pyrrolo[*a*]carbazoles **7** (**a**-**h**) *via* Michael addition of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** (**a**-**d**) to *trans*-β-nitrostyrenes **5** (**a**,**b**). However the reaction followed a different and unexpected course, affording aromatic carbocyclic products, benzo[*a*]carbazoles **8** (**a**-**h**) instead of the expected Michael adducts **6** (**a**-**h**), in fairly high yields (Scheme 4). The structures **6** (**a**-**h**) were easily ruled out on the basis of spectral data. The ^{1}H NMR spectrum of the observed product **8a** shows a singlet peak at δ 5.46 ppm owing to the presence of amino group. If the Michael adduct **6a** was formed, one would expect aliphatic protons instead of aromatic protons at C_3 and C_4 positions.

Thus we report a simple and environmentally safe route to the synthesis of a series of structurally novel and polyfunctionalized benzo[*a*]carbazole derivatives through an unexpected tandem Michael addition-cyclization reaction of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** with *trans*-β-nitrostyrene **5** using Et_3N as the base in DCM at 0°C. The reaction pathway involves a sequential vinylogous Michael addition, intramolecular cyclization followed by aromatization, resulting in multiple bond-formation events. This methodology has not been published elsewhere and demonstratesa unique path to polysubstituted benzo[*a*]carbazole derivatives.

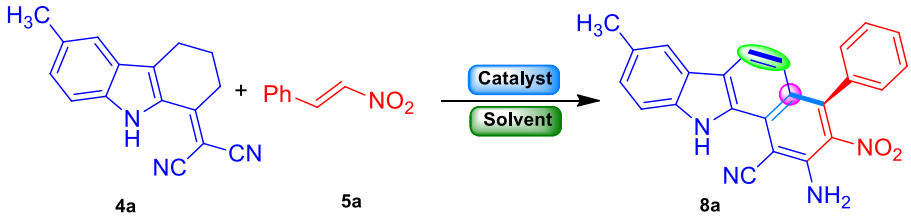


Scheme 4 Synthesis of 2-amino-3-nitro-4-aryl-11*H*-benzo[*a*]carbazol-1-carbonitrile **8**.

The reaction medium has been found to be one of the most important factors influencing the yield as well as the rate of the reaction. The model reaction was initiated between 1-

(dicyanomethylene)-6-methyl-2,3,4,9-tetrahydrocarbazole **4a** and *trans*-β-nitrostyrene **5a** in the presence of different catalysts and solvent systems to establish the feasibility of the strategy and to optimize the reaction condition (Table 1).

Table 1 Optimization of reaction conditions for the synthesis of **8a**[a]



Entry	Solvent	Catalyst	Time/T	Yield of **8a**[b]
1.	DCM	Catalyst-free	24/RT[c]	-
2.	DCM	NaOH (0.8 mmol)	18/RT	Trace
3.	DCM	KOH (0.7 mmol)	18/RT	42
4.	DCM	Morpholine (0.5 mL)	18/RT	40
5.	DCM	NH_4OAc (0.5 mmol)	14/RT	48
6.	DCM	Et_3N (0.2 mL)	10/RT	62
7.	DCM	Et_3N (0.3 mL)	10/RT	67
8.	DCM	Et_3N (0.4 mL)	8/RT	74
9.	DCM	Et_3N (0.5 mL)	7/RT	77
10.	**DCM**	**Et_3N (0.5 mL)**	**6/0°C**[d]	**84**
11.	DCM	Et_3N (0.6 mL)	6/0°C	83
12.	EtOH	Et_3N (0.5 mL)	6/0°C	52
13.	CH_3CN	Et_3N (0.5 mL)	6/0°C	29
14.	DMF	Et_3N (0.5 mL)	6/0°C	36
15.	$CHCl_3$	Et_3N (0.5 mL)	6/0°C	32

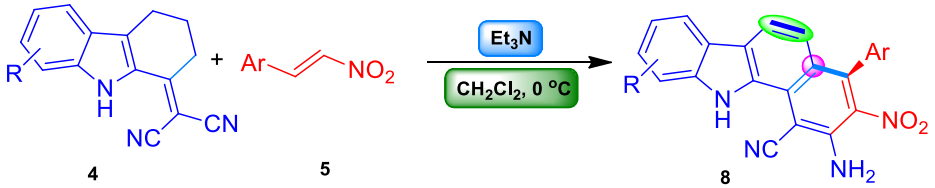
[a]The reaction conditions were as follows: **4a** (1.0 mmol), **5a** (1.0 mmol), Et_3N (0.5 mL), DCM (15 mL). [b]The isolated yield was obtained by silica gel column chromatography. [c]Room temperature. [d]Ice cold condition

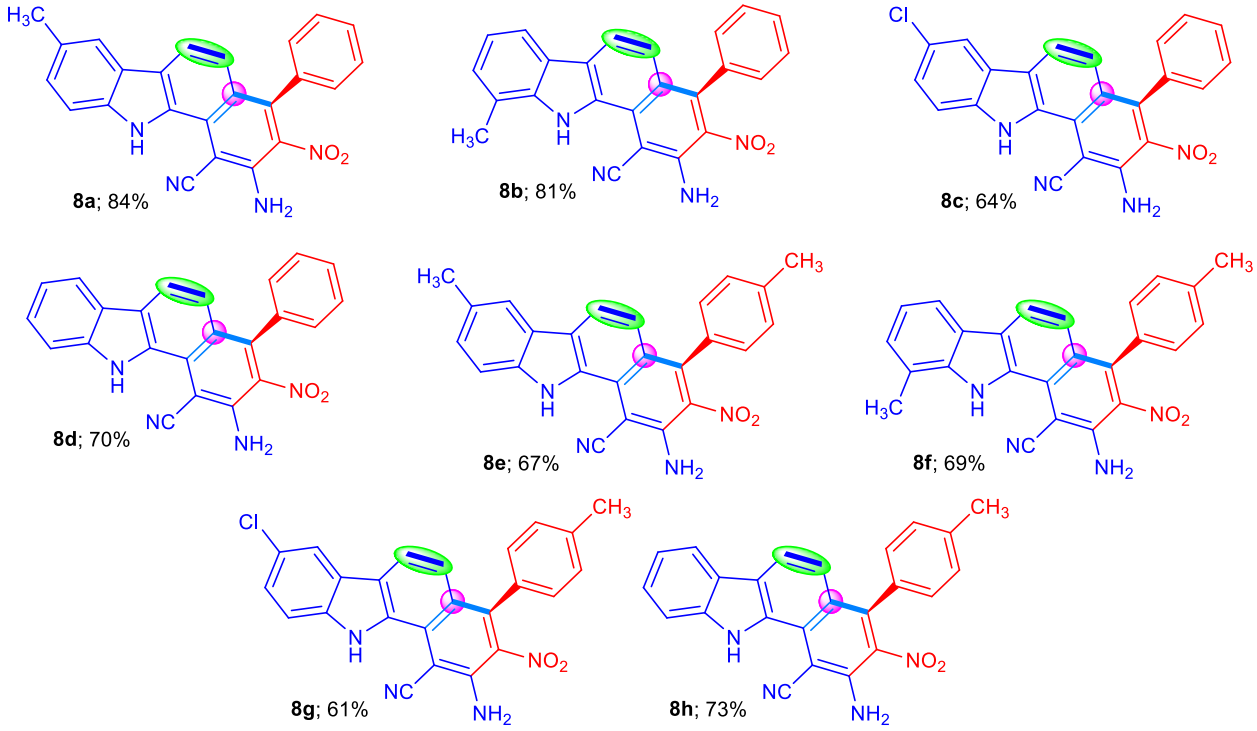
To probe the role of a catalyst, initially a blank reaction was conducted in DCM, however the reaction failed to give the product even after 24 h at room temperature (entry 1). It was

observed that the presence of a catalyst NaOH gave the cycloadduct **8a** in trace amount only (entry 2). Subsequently, various base catalysts, such as KOH, morpholine and ammonium acetate were tested for the reaction to promote tandem Michael addition and intramolecular cyclization and these bases gave **8a** in moderate amounts (entries 3-5). Surprisingly, the yield of the cyclic product **8a** was improved significantly when 0.2 mL of Et_3N was used (entry 6). The optimum quantity of Et_3N was screened and it was found that on increasing the amount of catalyst from 0.2 to 0.5 mL, the yield of the reaction increases gradually but beyond 0.5 mL there is no significant improvement in the rate or yield of the reaction (entries 7-11). Temperature and catalyst loading has an obvious influence on conversion to products. The best result was obtained with 0.5 mL catalyst loading at 0°C (entry 10). The solvent also had an important role on the reaction yield, thus similar reactions (entries 10-15) were conducted in DCM, EtOH, CH_3CN, DMF and $CHCl_3$, and DCM was obtained as the suitable solvent. The most encouraging result was obtained when the reaction was carried out in the presence of Et_3N (0.5 mL) as a catalyst in DCM at 0°C.

As illustrated by several representative examples in Table 2, the scope of this Michael reaction is broad. 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** (**a-d**) bearing various substituents reacted smoothly with β-nitrostyrenes **5** (**a**,**b**) to produce the corresponding products in good yields.

Table 2 Substrate scope of Michael addition-cyclization reaction





The structures of the synthesized compounds were consistent with their FT-IR, ^{1}H NMR,^{13}C NMR spectra and elemental analyses. The FT-IR spectral data of **8a** displayed prominent absorptions at 3464, 3406, 3377, 2205, 1549 and 1371 cm^{-1}were due to asymmetric NH_2, symmetric NH_2, indole NH, cyano, asymmetric and symmetric NO_2 groups, respectively. The ^{1}H NMR spectrum of **8a** exhibited a broad singlet for indole NH at δ 9.88 ppm. The aromatic protons appeared in the region of δ 7.91-7.35 ppm. The amino protons resonated as a singlet at δ 5.46 ppm and methyl protons at the C_8 position appeared as asinglet at δ 2.54 ppm. The ^{13}C NMR spectrum of **8a** displayed 24 resonances in agreement with the proposed structure. The exact mass of **8a** was observed to be 392.1241, which is very close to its theoretical value of 392.1270 $(C_{24}H_{16}N_4O_2)^{+}$. The molecular formula: identities of the other compounds **8** (**b-h**) were

established in a similar ways with all spectroscopic data readily assignable. The mechanistic abstract of formation of **8** was outlined in Fig.1.

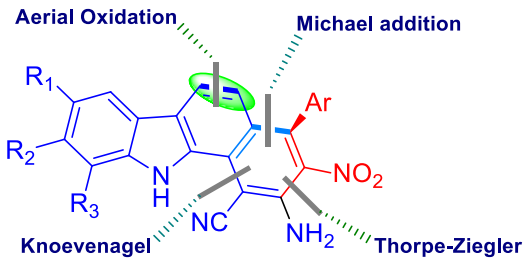
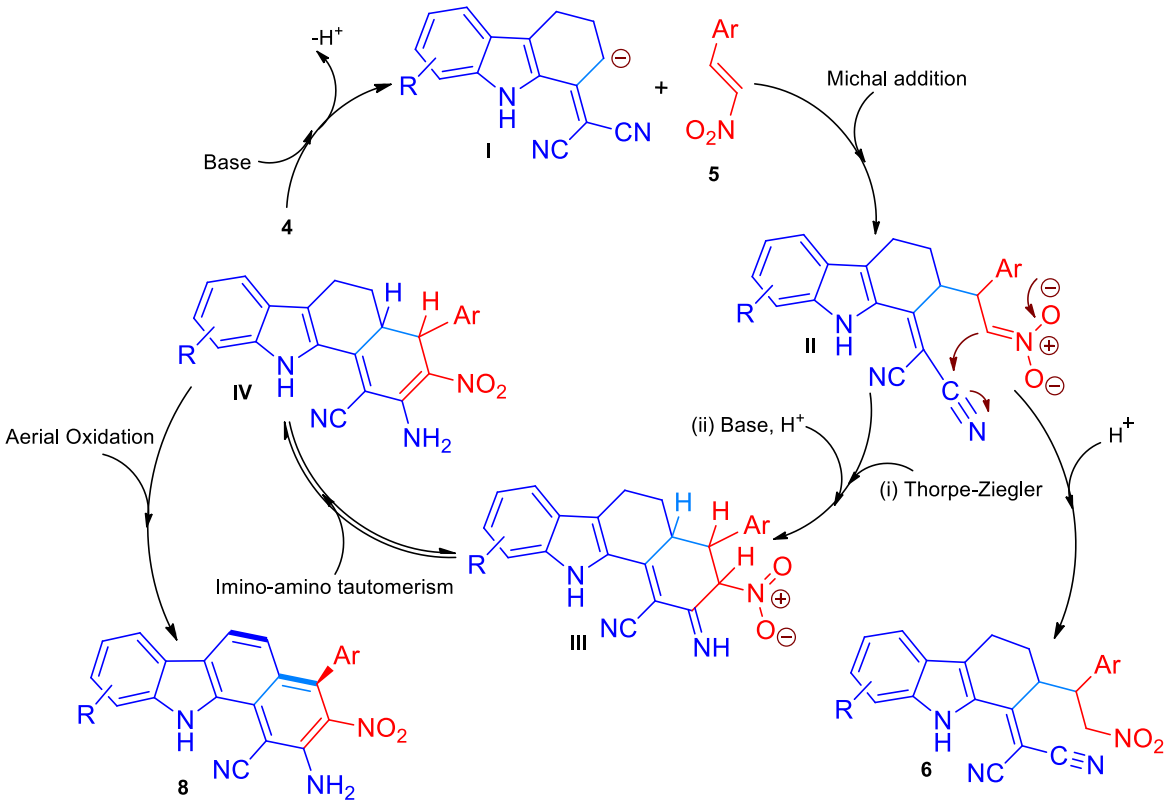


Fig.1. Outline of the mechanistic justification of **8**.

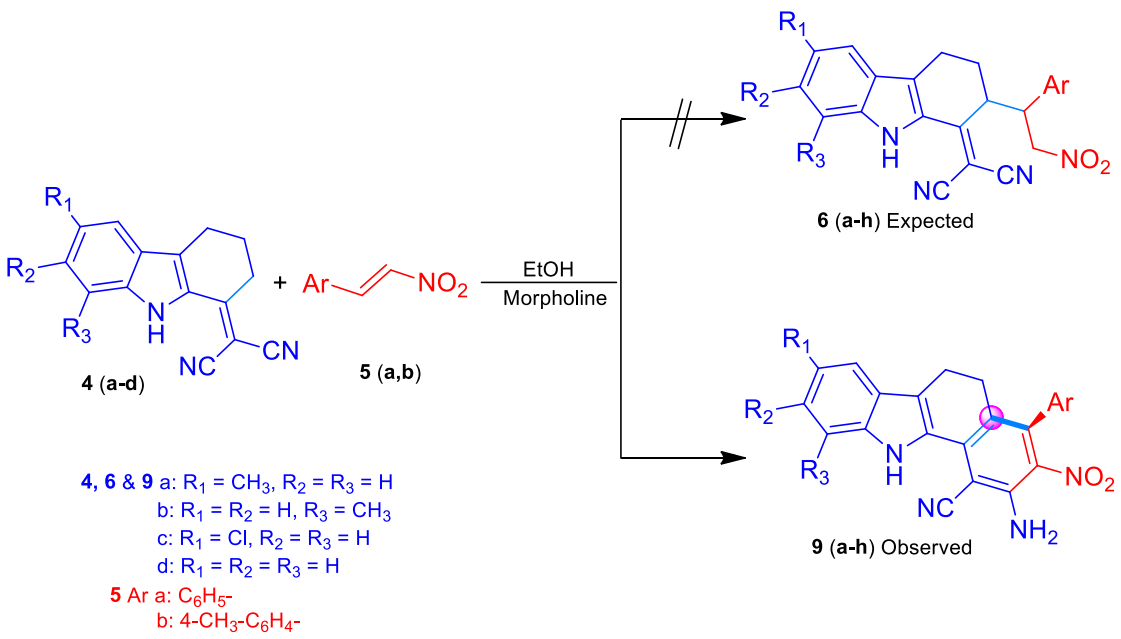
Mechanistic proposal for the formation of BCs **8** is outlined in Scheme 5. The base promoted Michael addition of vinylogous carbanion **I** derived from the synthon 1-(α,α-dicyanomethlene)-2,3,4,9-tetrahydrocarbazole **4** to β-nitrostyrene **5** forms an intermediate **II**, which is supposed to yield our expected final product **6** in the presence of base abstracted proton formed *in situ*. However our attempts to isolate the intermediate compound **6** were unsuccessful. Then the intermediate **II** undergoes intramolecular Thorpe-Ziegler ring closure affording the cyclized intermediate **III**. The subsequent imino-amino tautomeric shift followed by aerial oxidation yields the final stable observed compound **8** through the amino intermediate **IV**.



Scheme 5 Proposed mechanism for the formation of aromatized BCs **8**.

One of the challenges of modern synthesis is to create distinct types of novel complex scaffolds from identical reactants by careful choice ofcatalysts/conditions.[27]As a continuation of our interest in exploration of vinylogous Michael addition reaction and the chemistry of α,α-dicyanoalkenes, we envisaged that the direct synthesis of the Michael adduct **6** might be realized by a one-pot reaction of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** and *trans*-β nitrostyrene **5** under appropriate reaction conditions.

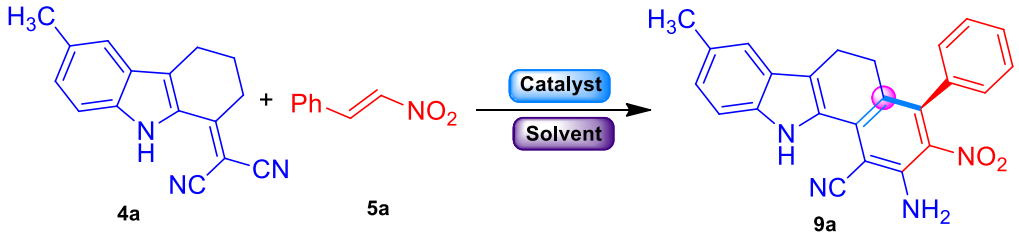
An attempted vinylogous Michael addition reaction of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** (**a**-**d**) with *trans*-β nitrostyrenes **5** (**a**,**b**) in ethanol in the presence of a catalytic amount of morpholine, failed to produce the Michael adducts **6** (**a**-**h**), but surprisingly this did give an unexpected dihydro carbocyclic product **9** (**a**-**h**), confirmed by different spectral techniques and X-ray diffraction studies. Based on the spectral and crystal data, the obtained compound was identified as 2-amino-3-nitro-4-aryl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **9**. The synthetic approach adopted to obtain the novel compounds is depicted in Scheme 6.



Scheme 6 Synthesis of 2-amino-3-nitro-4-aryl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile **9**.

To optimize the reaction condition, a set of base catalysts and solvent systems were studied and the results are summarized in Table 3.

Table 3 Catalyst- and solvent-screen for the synthesis of **9a**[a]



Entry	Solvent	Catalyst	Time/T	Yield of **9a**[b]
1.	EtOH	Catalyst-free	24/RT[c]	-
2.	EtOH	Et_3N (0.2 mL)	24/RT	Trace
3.	EtOH	Et_3N (0.2 mL)	12/R[d]	20
4.	EtOH	K_2CO_3 (0.1 mmol)	8/R	37
5.	EtOH	NaOH (0.8 mmol)	8/R	25
6.	EtOH	DABCO (0.2 mmol)	8/R	48
7.	EtOH	Piperidine (0.2 mL)	8/R	58

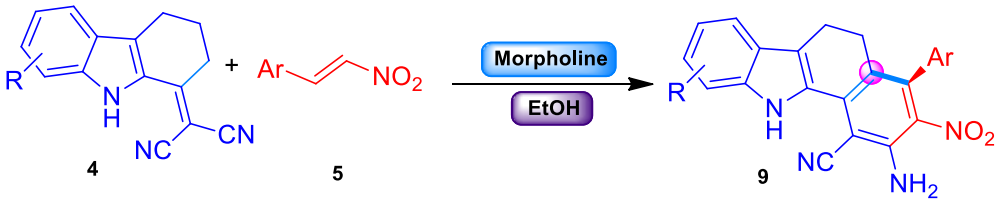
8.	**EtOH**	**Morpholine (0.2 mL)**	**6/R**	**90**
9.	EtOH	Morpholine(0.15 mL)	6/R	77
10.	EtOH	Morpholine(0.1 mL)	6/R	68
11.	MeOH	Morpholine(0.2 mL)	6/R	70
12.	CH_3CN	Morpholine(0.2 mL)	6/R	40
13.	DMF	Morpholine(0.2 mL)	6/R	45
14.	DCM	Morpholine(0.2 mL)	6/R	40
15.	1,4-Dioxane	Morpholine(0.2 mL)	6/R	30

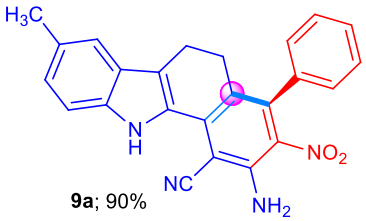
[a]The reaction conditions were as follows: **4a** (1.0 mmol), **5a** (1.0 mmol), morpholine (0.2 mL), EtOH (20 mL). [b]The isolated yield was obtained by silica gel column chromatography. [c]Room temperature. [d]Reflux

Initially, the reaction was performed in ethanol in the absence of a catalyst at room temperature for 24 h and we did not observe any product formation (entry 1). The reaction was very sluggish and incomplete even after 24 h of stirring in the presence of triethylamine as catalyst (entry 2). It was observed that the same reaction under reflux condition resulted in an increasein the yield of 20%. In order to further enhance the rate of conversion, screening other organic bases such as K_2CO_3, NaOH and DABCO, but the yield did not increase significantly (entries 4-6). With piperidine as the base a moderate yield of around 60% could be achieved (entry 7). Remarkably, when the reaction mixture was refluxed in the presence of 0.2 mL of morpholine, it afforded the desired product **9a** in 90% yield (entry 8). It was noted that the yield of the product **9a** was influenced by the amount of the catalyst (entries 9 & 10). From these observations, it seems that morpholine is the optimal catalyst. To determine a suitable solvent system, similar reactions (entries 10-15) were conducted in EtOH, MeOH, CH_3CN, DMF, DCM and 1,4-dioxane under identical conditions and the highest yields obtained in ethanol. Thus the best yield of 90% for the reaction between 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole and nitrostyrene was obtained by using morpholine as the base in refluxing ethanol.

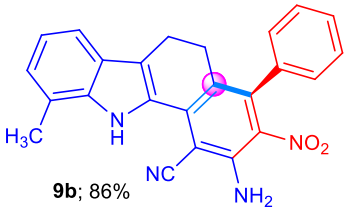
To explore the synthetic scope and the generality of the present protocol, we use differently substituted1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** (**a-d**) and β-nitrostyrenes **5** (**a**,**b**) which gave the corresponding highly substituted dihydrobenzo[*a*]carbazoles **9** (**a-h**) in good yield as shown in Scheme 6 (Table 4).

Table 4 Substrate scope of dihydrobenzo[*a*]carbazoles **9** *via* tandem Michael addition reaction

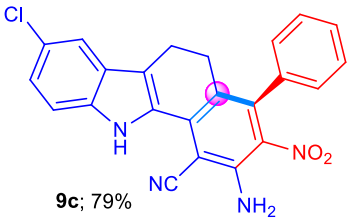




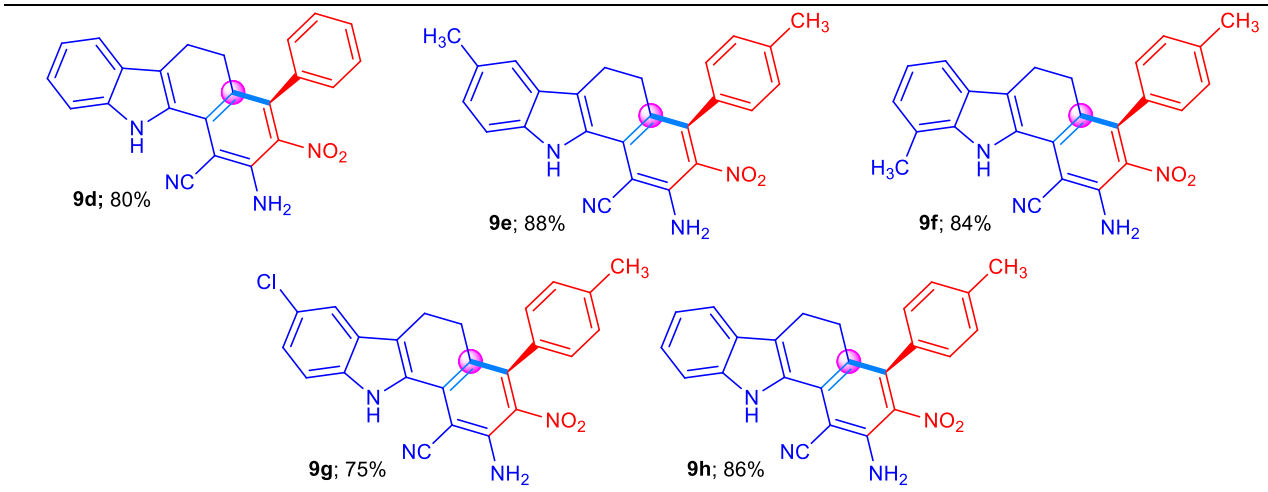
9a; 90%



9b; 86%



9c; 79%



The structural analyses of **9** (**a-h**) were made by FT-IR, ^{1}H NMR, ^{13}C NMR spectral studies and elemental analyses. The structures of the representative compounds such as **9b** and **9d** were further confirmed unambiguously by single crystal X-ray diffraction analysis (Fig. 2, see in the ESI). The FT-IR spectral data of **9a** displayed characteristic peaks at 3450, 3385, 2207, 1547 and 1325 cm^{-1} which are indicative of the asymmetric NH_2, symmetric NH_2 overlapped with indole NH, cyano, asymmetric and symmetric NO_2 groups, respectively. The ^{1}H NMR spectrum of **9a** exhibited a broad singlet for indole NH at δ 9.25 ppm. The aromatic protons appeared in the region of δ 7.46-7.15 ppm. The amino protons resonated as a singlet at δ 5.71 ppm, while the aliphatic protons appeared as two multiplets centered at δ 2.81 and δ 2.59 ppm respectively and methyl protons at C_8 position appeared as a singlet at δ 2.44 ppm. The ^{13}C NMR spectrum of **9a** displayed 24 resonances in agreement with the proposed structure. The HRMS spectrum of **9a** showed the molecular ion peak at 394.1392. The identities of the other compounds **9** (**b-h**) were established in a similar ways with all spectroscopic data readily assignable.

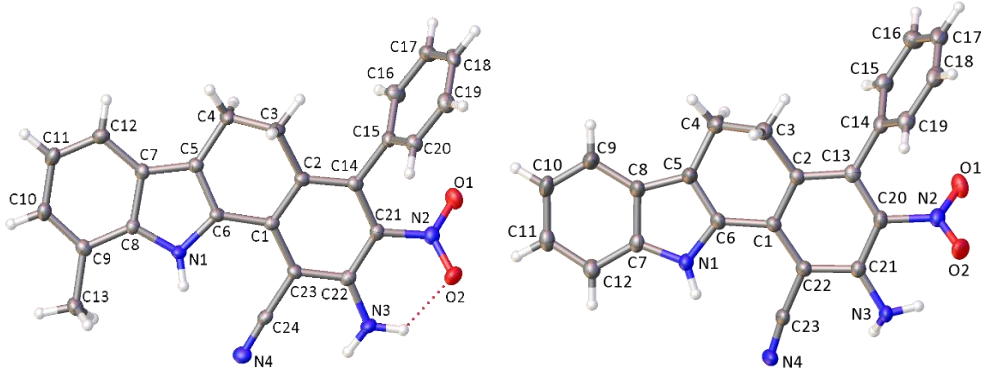
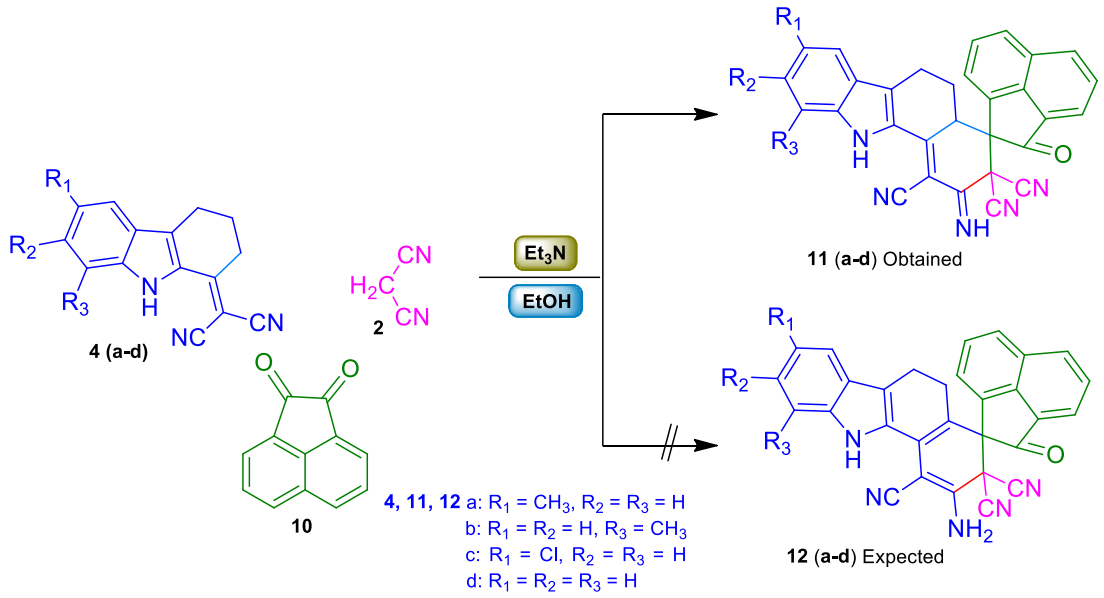


Fig.2. Crystal structures of **9b** (left) and **9d** (right) with the atomic numbering scheme depicted. Ellipsoids are displayed at the 50% probability level.

With the assistance of catalytic amount of tertiary and secondary amines, these divergent protocols provides an efficient, environment friendly and straight forward methodology for the preparation of biologically valuable benzocarbazoles **8** and dihdrobenzocarbazoles **9** in good yields.

After the successful synthesize of functionalized BCs and BDHCs using α,α-dicyanomethylidene carbazoleas synthon by catalytic divergent-tandem Michael reaction, we were prompted to extend the scope of this protocol to the synthesis of complex spirobenzocarbazole hybrids.

In the present study, we have reported an efficient protocol for the solution phase synthesis of new spiroacenaphthylene **11** through the three component assembling of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (**a-d**) with malononitrile **2** and acenaphthequinone **10** in the presence of a mild catalyst Et_3N. On the basis of spectral data the expected amino structure **12** was easily ruled out. However, to our surprise the sole imino products 2-imino-1'-oxo-5,6-dihydro-11*H*-spiro(acenaphthylene-8',4-benzo[*a*]carbazole)-1,3,3-tricarbonitrile **11** (**a-d**) were obtained (Scheme 7).



Scheme 7 2-Imino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **11**.

A systematic study was performed to check the effect of different catalysts and solvents and the results are summarized in Table 5. Initially, the reaction was carried out by taking the synthon **4a**, malononitrile **2** and acenaphthequinone **10** as model substrates in EtOH at room temperature without using any catalyst and we did not observe any of the three component product even after 12 h (entry 1). However, the same reaction mixture in the presence of bases such as K_2CO_3 and NaOH provided the formation of the desired product in 19% and 27% yield, respectively (entries 2 & 3). The yield was improved significantly when morpholine and DABCO were used as bases (entries 4 & 5). The reaction was then attempted using Et_3N as the catalyst in EtOH. The reaction was complete in 5 h and gave 83% yield of **11a** after a simple workup (entry 6). Consequently, the same reaction was carried out in different solvents such as ethanol, methanol, DMF, dioxane and acetonitrile to examine the effect of solvents on the product formation (entries 6-10). It was observed that the reaction performed in ethanol gave much better results as compared to other solvents. Taking all these observations into consideration, we found Et_3N in ethanol were the best conditions for the present protocol.

Table 5 Optimization of the reaction conditions of **11a**[a]

Entry	Solvent	Catalyst	Time (h)	Yield(%)[b]
1.	EtOH	Catalyst-free	12	–
2.	EtOH	K_2CO_3 (0.1 mmol)	12	19
3.	EtOH	NaOH (0.8 mmol)	10	27
4.	EtOH	Morpholine (0.1 mmol)	10	34
5.	EtOH	DABCO (0.2 mmol)	8	46
6.	**EtOH**	**Et_3N** (0.1 mmol)	**5**	**83**
7.	MeOH	Et_3N (0.1 mmol)	5	71
8.	DMF	Et_3N (0.1 mmol)	5	48
9.	1,4-Dioxane	Et_3N (0.1 mmol)	5	64
10.	CH_3CN	Et_3N (0.1 mmol)	5	52

[a]The reaction conditions were as follows: **4a** (1.0 mmol),**2** (1.0 mmol), **10** (1.0 mmol), Et_3N

(0.1 mmol), EtOH (15 mL), [b]The isolated yield was obtained by silica gel column chromatography.

Next, to delineate the scope of this approach particularly with regard to library construction, this method was evaluated using substituted synthons, 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazoles **4** (**a-d**) and the corresponding products **11** (**a-d**) were obtained in good yields under similar conditions (Table 6).

Table 6 Synthesis of spiroacenaphthylene-benzo[*a*]carbazole derivatives **11**

Entry	R_1	R_2	R_3	Product	Time (h)	Yield[a](%)
1.	CH_3	H	H	**11a**	5	83
2.	H	H	CH_3	**11b**	5	79
3.	Cl	H	H	**11c**	5.5	73
4.	H	H	H	**11d**	5	80

The reaction procedure is very simple. A nearly homogeneous system was formed at the beginning of the reaction. After the reaction was complete, a yellow precipitate was obtained as the product which could be rendered very pure by simple filtration. Finally, the structure of this was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analyses. This novel protocol is a muticomponent route, which is operational simple, avoid the use of conventional volatile organic solvents, has no waste formation and allows the easy separation of highly pure products.

The FT-IR spectrum of compound **11a** showed stretching bands at 3451, 3294, 2210 and 1722 cm^{-1} due to indole NH, imino NH, cyano and carbonyl groups respectively. The ^{1}H NMR of **11a** displayed two broad singlets at δ 11.37 and δ10.95 ppm which indicated the presence of indole NH and imino NH protons, respectively. The peaks in the region of δ 8.50-7.22 ppm were observed for aromatic protons. The methylene protons at C_6 were visible as a multiplet at δ 2.91-2.86 ppm. A sharp singlet at δ 2.32 ppm accounted for the methyl protons at C_8 position and, the methylene protons of C_{5a} and C_{5b} appeared as two multiplets centered at δ 1.45 and δ 1.22 ppm respectively. The ^{13}C NMR spectrum of **11a** displayed 31 resonance signals in agreement with the proposed structure. The presence of a molecular ion peak at m/z 477.1554 in the mass

spectrum which further supported the formation of the product **11a**. The selected ^{1}H and ^{13}C chemical shifts of **11a** were shown in Fig. 3.

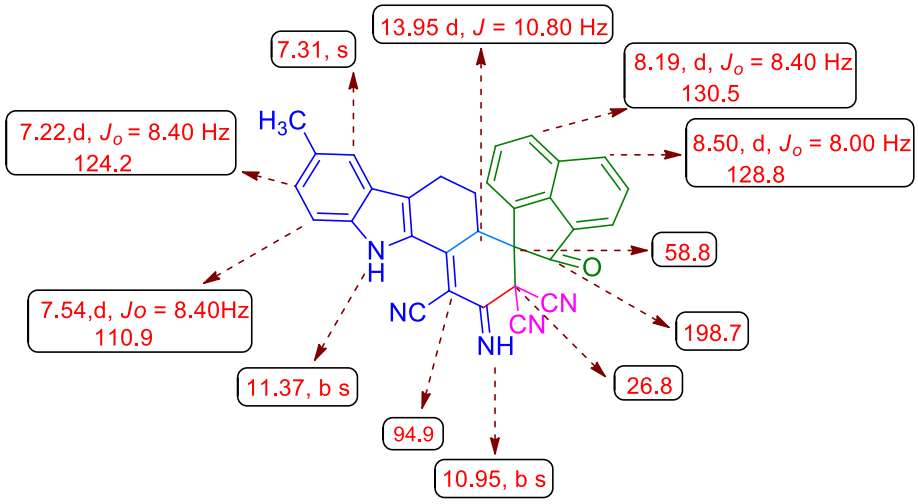
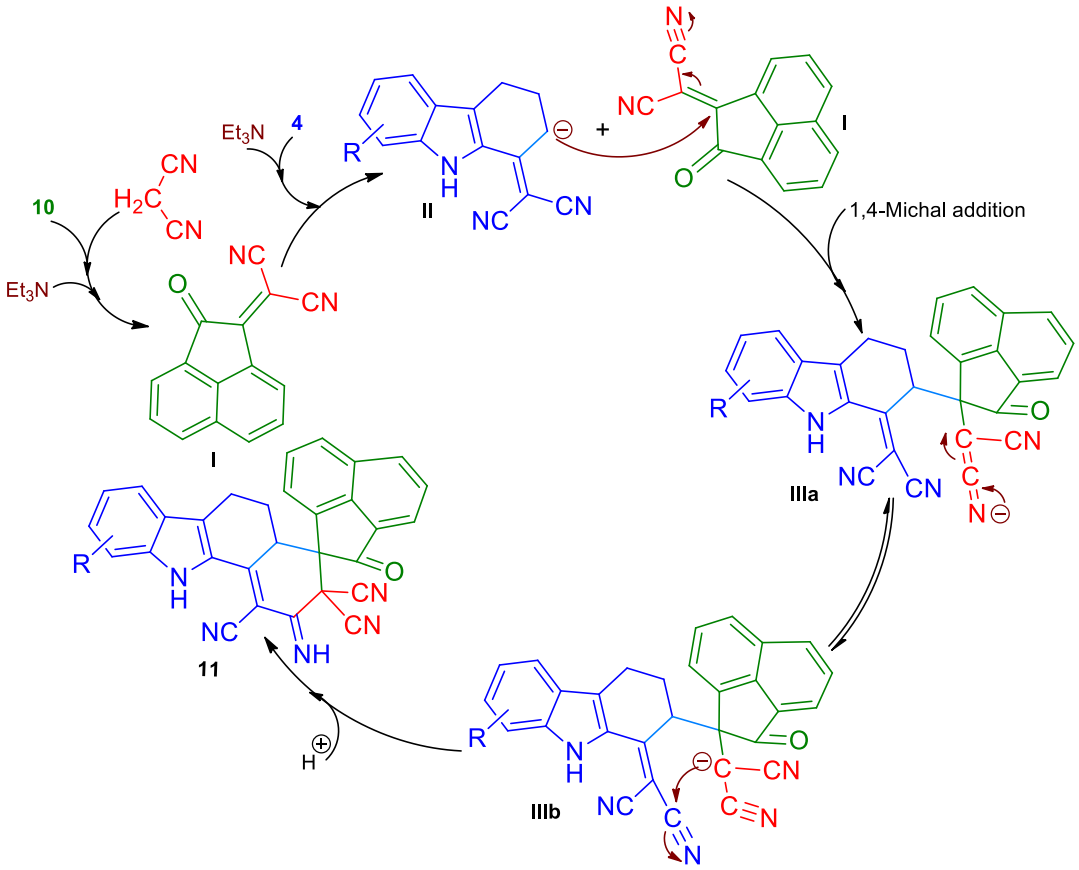


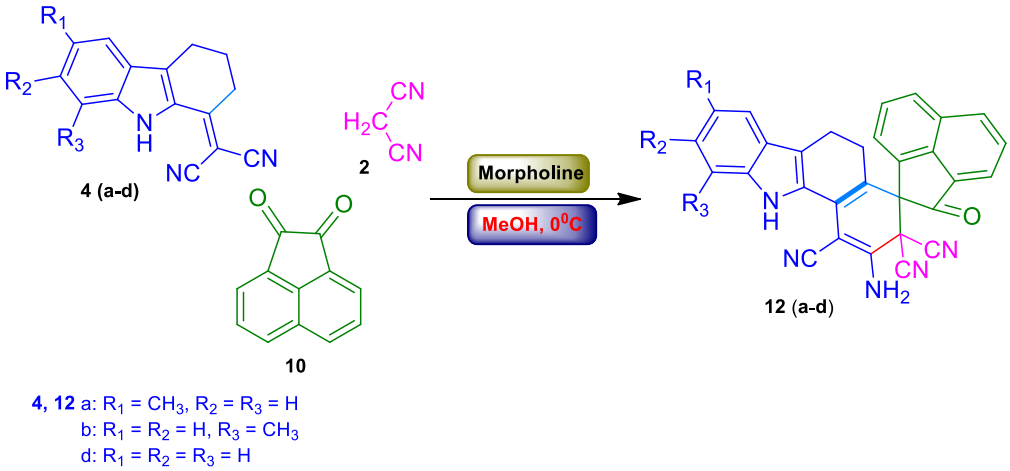
Fig. 3. Selected ^{1}H, ^{13}C chemical shifts of **11a**.

To explain the mechanism of these multicomponent reactions, we propose the following reaction course (Scheme 8). The base promoted Knoevenagel condensation between malononitrile and acenaphthenequinone **10** takes place with the formation of an unsaturated nitrile intermediate **I**. The regiospecific 1,4-Michael addition of vinylogous carbanion **II** derived from the synthon 1-(α,α-dicyanomethlene)-2,3,4,9-tetrahydrocarbazole **4** to Knoevenagel adduct affords the intermediate **IIIa**, which is stabilized through its carbanion form **IIIb**. Subsequently, this carbanion intermediate **IIIb** on intramolecular nucleophilic cycloaddition to the CN group attached to alkene resulted in the formation of the final imino product **11**.



Scheme 8 Plausible mechanism for the formation of **11**.

The intermediacy of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** offers an additional opportunity to increase the diversity of the spiroacenaphthylene-benzo[*a*]carbazolehybrids *via* a catalytic divergent protocol. To our delight, the tandem secondary amine, morpholine controlled three component reaction of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (**a-d**) with malononitrile **2** and acenaphthequinone **10** in MeOH satisfied these requirements, affording amino functionalized spiroacenaphthylene-benzo[*a*]carbazoles **12** (**a-d**) with good yields (Scheme 9).



Scheme 9 2-Amino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile **12**.

The reaction pathway, substrate scope, and product regioselectivity are similar to that proposed in the previous scheme. It may be noted that the variation of either catalyst or condition exerted an influence in this reaction and allowed the synthesis of amino substituted spiroacenaphthylene-benzo[*a*]carbazole **12**.

The structures of the synthesized compounds were characterized using elemental analysis, FT-IR, and ^{1}H NMR spectroscopic analyses. The ^{1}H NMR spectra of the products confirmed the formation of amino functionalized spiro compounds. The ^{1}H NMR spectrum of **12a** showed a singlet at δ 5.17 ppm which accounted to NH_2 protons. In contrast, if the imino functionalized spiro compound **11a** had formed, an allylic proton at C_{4a} position would have appeared as a doublet in the ^{1}H NMR spectrum. The formation of products **12** was also elucidated with the help of FT-IR. In the FT-IR spectrum of **12a**, the stretching vibrations at 3444 and 3365 cm^{-1} can be readily assigned to asymmetric and symmetric NH_2 group.

Conclusions

In conclusion, a product-switchable amine catalysed Michael addition of α,α-dicyanomethylidenecarbazoles to β-nitrostyrenes has been developed that enables the efficient and divergent synthesis of two types of benzo[*a*]carbazole derivatives, BCs and BDHCs under different conditions. Additionally, the selective conversion of α,α-dicyanomethylidenecarbazoles to imino and amino functionalized spiro[acenaphthylene-8',4-benzo[*a*]carbazole] derivatives by a three component reaction has been achieved. The divergent reaction pathways of the dicyanoalkenes are precisely controlled by a simple change of reaction solvents/condition or amine catalysts to selectively afford diverse benzo[*a*]carbazole collection.

Experimental section

General: All the chemicals were bought from Sigma-Aldrich and Merck and were utilized for the process without further purification. Melting points (m.p.) were determined on a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. They are expressed in degree centigrade (°C). FT-IR spectra were recorded on Avatar Model FT-IR(4000–400 cm^{-1}) spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Agilent- 400 MHz (^{1}H) and 100 MHz (^{13}C) spectrometers respectively in $CDCl_3$ using TMS (tetramethylsilane) as internal reference; chemical shifts are expressed in parts per million (ppm); coupling constants (*J*) are reported in hertz (Hz) and the terms J_o and J_m refer to ortho coupling constant and meta coupling constant. The signals were characterized as s (singlet), d (doublet), t (triplet), m (multipiet), bs (broad singlet) and dd (doublet, and doublet). Microanalyses were carried out using Vario EL III model CHNS analyzer (Vario, Germany). When known compounds had to be prepared according to literature procedures and pertinent references are given. The purity of the products was tested by TLC plates coated with silica gel-G using petroleum ether and ethyl acetate in the ratio of 1:1 as developing solvents.

General procedure for the preparation of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole (**4**). A mixture of 2,3,4,9-tetrahydrocarbazol-1-one **1** (1.0 mmol), malononitrile **2** (1.0 mmol), ammonium acetate **3** (1.2 mmol) and four drops of acetic acid in 10 mL of toluene was refluxed at 120℃ for 6 h. On cooling, the precipitate that formed was filtered off, washed with petroleum ether and dried. The crude product thus obtained was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (99:1) to yield the corresponding product 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4**.

1-(Dicyanomethylene)-6-methyl-2,3,4,9-tetrahydrocarbazole (**4a**). Pale yellow solid; yield: 172 mg (70%); m.p. 199-201 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3381 (NH), 2211(CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.25 (br s, 1H, N_9-H), 7.38 (s, 1H, C_5-H), 7.30-7.24 (m, 2H, C_8 & C_7-H), 2.99-2.97 (m, 4H, C_4 & C_3-2H), 2.43 (s, 3H, C_6-CH_3), 2.10-2.07 (m, 2H, C_2-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.2 (C_1), 138.0 (C_{9a}), 131.2 (C_{8a}), 130.9 (C_6), 130.3 (C_{4b}), 128.5 (C_7), 125.6 (C_5), 120.2 (C_{4a}), 116.5 (C_8), 113.6 (CN & CN), 112.0 (C_1'), 31.4 (C_2), 23.4 (C_4), 21.9 (C_3), 21.3 (CH_3); Anal.calcd. for $C_{16}H_{13}N_3$:C, 77.71; H, 5.30; N, 16.99; Found: C, 77.80; H, 5.26; N, 16.92 %.

1-(Dicyanomethylene)-8-methyl-2,3,4,9-tetrahydrocarbazole (**4b**). Pale yellow solid; yield: 160 mg (65%); m.p. 197-199°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3385 (NH), 2209 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.33 (br s, 1H, N_9-H), 7.47 (d, 1H, C_5-H, J_o = 8.40 Hz), 7.25-7.21 (m, 1H, C_7-H), 7.09 (t, 1H, C_6-H, J = 7.60 Hz), 3.02-2.96 (m, 4H, C_4 & C_3-2H), 2.48 (s, 3H, C_8-CH_3), 2.13-2.07 (m, 2H, C_2-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.7 (C_1), 138.3 (C_{9a}), 131.0 (C_{8a}), 130.5 (C_6), 130.7 (C_{4b}), 128.9 (C_7), 125.2 (C_5), 121.0 (C_{4a}), 116.7 (C_8), 113.8 (CN & CN), 112.4 (C_1'), 31.6 (C_2), 23.5 (C_4), 21.6 (C_3), 21.5 (CH_3); Anal.calcd. for $C_{16}H_{13}N_3$:C, 77.71; H, 5.30; N, 16.99; Found: C, 77.62; H, 5.34; N, 16.93 %.

1-(Dicyanomethylene)-6-chloro-2,3,4,9-tetrahydrocarbazole (**4c**). Pale yellow solid; yield: 149 mg (56%); m.p. 198-200°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3363 (NH), 2205(CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.36 (br s, 1H, N_9-H), 7.59 (s, 1H, C_5-H), 7.36-7.24 (m, 2H, C_8 & C_7-H), 3.01-2.95 (m, 4H, C_4 & C_3-2H), 2.14-2.07 (m, 2H, C_2-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 160.3 (C_1), 138.3 (C_{9a}), 131.3 (C_{8a}), 131.0 (C_6), 130.5 (C_{4b}), 128.7 (C_7), 125.4 (C_5),

120.3 (C_{4a}), 116.4 (C_8), 113.7 (CN & CN), 112.2 (C_1'), 31.3 (C_2), 23.5 (C_4), 21.7 (C_3); Anal. calcd. for $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.77; N, 15.70; Found: C, 67.39; H, 3.72; N, 15.77 %.

1-(Dicyanomethylene)-2,3,4,9-tetrahydrocarbazole (4d). Pale Yellow solid; yield: 170 mg (73%); m.p. 196-198°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3366 (NH), 2216 (CN); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 10.8 (br s, 1H, N_9-H), 7.69-7.63 (m, 2H, C_8 & C_5-H), 7.41-7.37 (t, 1H, C_6-H, J_o= 7.80 Hz), 7.15-7.11 (t, 1H, C_7-H), 2.96-2.94 (m, 4H, C_4 & C_3-2H), 2.00 (m, 2H, C_2-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 161.0 (C_1), 140.5 (C_{9a}), 130.6 (C_{8a}), 128.4 (C_{4b}), 128.1 (C_7), 125.2 (C_6), 120.9 (C_5), 120.7 (C_{4a}), 114.9 (CN), 114.5 (CN), 113.7 (C_8), 69.5 (C_1'), 31.2 (C_2), 23.1 (C_4), 21.2 (C_3); Anal. calcd. for $C_{15}H_{11}N_3$:C, 77.23; H, 4.75; N, 18.01; Found: C, 77.31; H, 4.71; N, 18.10 %.

The synthesis of 2-amino-3-nitro-4-aryl-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8**). To a glass vial equipped with a magnetic stir bar were charged with 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol), nitrostyrene **5** (1.0 mmol) and catalytic amount of triethylamine (0.5 mL) in 15 mL of dichloromethane and stirred at 0°C for 6 h. The progress of the reaction was monitored by TLC. After completion of the reaction crude was purified by column chromatography over silica gel to give the pure compound **8**.

2-Amino-8-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8a**). Orange solid; yield: 329 mg (84%); m.p. 287-289°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3464 (asym NH_2), 3406 (sym NH_2), 3377 (indole NH), 2205 (CN), 1549 (asym NO_2), 1371 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.88 (br s, 1H, N_{11}-H), 7.91 (d, 1H, C_6-H, J_o = 8.80 Hz), 7.87 (s, 1H, C_7-H), 7.54-7.51 (m, 4H, C_5, C_6', C_2' & C_4'-H), 7.37-7.35 (m, 4H, C_{10}, C_5', C_3' & C_9-H), 5.46 (s, 2H, C_2-NH_2), 2.54 (s, 3H, C_8-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.2 (C_2), 137.6 (C_{10a} & C_{11a}), 134.4 (C_4 & C_1'), 131.4 (C_3), 130.1 (C_{6b} & C_8), 129.0 (C_5' & C_3'), 128.7 (C_6' & C_2'), 128.5 (C_4'), 123.8 (C_7 & C_9), 123.3 (C_5), 122.5 (C_6 & C_{4a}), 120.4 (C_{11b}), 120.0 (C_{10}), 119.5 (CN), 118.9 (C_{6a}), 111.4 (C_1), 21.4 (CH_3); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{24}H_{16}N_4O_2$: 392.1270; Found: 392.1241; Anal. calcd. for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28; Found: C, 73.55; H, 4.16; N, 14.21 %.

2-Amino-10-methyl-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8b**). Orange solid; yield: 317 mg (81%); m.p. 286-288°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3456 (asym NH_2), 3383 (sym NH_2 & indole NH) 2205 (CN), 1545 (asym NO_2), 1360 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.97 (br s, 1H, N_{11}-H), 7.93 (d, 2H, C_6 & C_5-H, J_o = 8.80 Hz), 7.52-7.51 (m, 3H, C_7, C_6' & C_2'-H), 7.37-7.33 (m, 3H, C_5', C_3' & C_4'-H), 7.26-7.20 (m, 2H, C_9 & C_8-H), 5.46 (s, 2H, C_2-NH_2), 2.69 (s, 3H, C_{10}-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 137.4 (C_{6b}), 137.3 (C_2), 132.8 (C_{11a}), 132.3 (C_1'), 129.6 (C_4), 126.6 (C_3), 125.3 (C_{10a}), 124.3 (C_5'& C_3'), 124.0 (C_6' & C_2'), 123.8 (C_4'), 122.6 (C_{10}), 119.0 (C_8), 118.6 (C_9), 117.8(C_5), 116.8 (CN), 115.6 (C_6), 115.3 (C_7), 114.7 (C_{4a}), 114.0 (C_{11b}), 106.7 (C_{6a}), 81.3 (C_1), 16.7 (CH_3); Anal. calcd. for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28; Found: C, 73.54; H, 4.15; N, 14.22 %.

2-Amino-8-chloro-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8c**). Orange solid; yield: 263 mg (64%); m.p. 278-280°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3460 (asym NH_2), 3386 (sym NH_2 & indole NH), 2212 (CN), 1541 (asym NO_2), 1369 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.99 (br s, 1H, N_{11}-H), 8.05 (s, 1H, C_7-H), 7.88 (d, 1H, C_6-H, J_o = 9.20 Hz), 7.58 (d, 3H, C_5, C_6' & C_2'-H, J_o = 8.80 Hz), 7.50-7.44 (m, 3H, C_{10}, C_5' & C_3'-H), 7.37-7.36 (m, 2H, C_4' & C_9-H), 5.48 (s, 2H, C_2-NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.1 (C_2), 129.2 (C_{10a}), 129.0 (C_{11a}), 128.7 (C_2'), 128.6 (C_4), 128.4 (C_3), 127.9 (C_{6b}), 127.3 (C_5' & C_3'), 126.3 (C_6' & C_1'), 125.7 (C_4'), 123.5 (C_8), 122.7 (C_9), 121.0 (C_7), 120.1 (C_5), 119.4 (C_6), 119.2 (C_{4a}), 118.6 (CN), 113.1 (C_{10} & C_{11b}), 112.9 (C_{6a} & C_1); Anal. calcd. for $C_{23}H_{13}ClN_4O_2$: C, 66.92; H, 3.17; N, 13.57; Found: C, 66.83; H, 3.21; N, 13.50 %.

2-Amino-3-nitro-4-phenyl-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8d**). Orange solid; yield: 264 mg (70%); m.p. 284-286°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3456 (asym NH_2), 3383 (sym NH_2 & indole NH), 2205 (CN), 1544 (asym NO_2), 1359 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.98 (br s, 1H, N_{11}-H), 8.10 (d, 1H, C_6-H, J_o = 7.60 Hz), 7.93 (d, 1H, C_7-H, J_o = 8.80 Hz), 7.65 (d, 2H, C_6' & C_2'-H, J_o = 7.60 Hz), 7.57-7.52 (m, 2H, C_{10} & C_5-H), 7.38-7.31 (m, 2H, C_5' & C_3'-H), 7.24-7.21 (m, 2H, C_8 & C_9-H), 7.15 (t, 1H, C_4'-H, J = 7.60 Hz), 5.47 (s, 2H, C_2-NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.3 (C_2), 142.1 (C_{10a}), 139.3 (C_{11a}), 137.8 (C_1'), 137.2 (C_4), 134.3 (C_3), 129.5 (C_5' & C_3'), 127.9 (C_6' & C_2'), 127.1 (C_4'), 123.9 (C_{6b}), 121.7 (C_9), 121.4 (C_7), 120.6 (C_5), 120.5 (C_8), 120.4 (C_6), 119.5 (C_{4a}), 118.7 (CN), 112.4 (C_{11b}), 112.0 (C_{10}), 111.8

(C_{6a}), 86.1 (C_1); Anal. calcd. for $C_{23}H_{14}N_4O_2$: C, 73.01; H, 3.73; N, 14.81; Found: C, 73.10; H, 3.69; N, 14.74 %.

2-Amino-8-methyl-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8e**). Orange solid; yield: 272 mg (67%); m.p. 279-281°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3430 (asym NH_2), 3376 (sym NH_2 & indole NH) 2207 (CN), 1551 (asym NO_2), 1352 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.87 (br s, 1H, N_{11}-H), 7.91 (d, 1H, C_6-H, J_o = 8.80 Hz), 7.87 (s, 1H, C_7-H), 7.54 (d, 1H, C_5-H, J_o = 8.60 Hz), 7.37-7.32 (m, 3H, C_{10}, C_6' & C_2'-H), 7.24-7.23 (m, 3H, C_9, C_5' & C_3'-H), 5.43 (s, 2H, C_2-NH_2), 2.55 (s, 3H, C_8-CH_3), 2.46 (s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.2 (C_{6b}), 142.1 (C_2), 139.0 (C_{10a}), 138.8 (C_4), 131.3 (C_3), 131.0 (C_1'), 129.3 (C_{10a}), 128.9 (C_4'), 127.8 (C_5' & C_3'), 127.3 (C_6' & C_2'), 125.7 (C_{10}), 123.9 (C_8), 121.8 (C_9), 121.5 (C_5), 120.9 (C_6), 120.7 (C_{4a}), 119.6 (C_7), 118.8 (CN), 118.0 (C_{11b}), 117.4 (C_{6a}), 85.9 (C_1), 21.3 (C_4'-CH_3), 16.5 (C_8-CH_3); Anal. calcd. for $C_{25}H_{18}N_4O_2$: C, 73.88; H, 4.46; N, 13.78; Found: C, 73.95; H, 4.42; N, 13.85 %.

2-Amino-10-methyl-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8f**). Orange solid; yield: 280 mg (69%); m.p. 276-278°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3436 (asym NH_2), 3380 (sym NH_2 & indole NH), 2205 (CN), 1548 (asym NO_2), 1350 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.93 (br s, 1H, N_{11}-H), 7.93-7.89 (m, 2H, C_6 & C_5-H), 7.33 (d, 3H, C_7, C_6' & C_2'-H, J_o = 8.00 Hz), 7.25 (d, 3H, C_9, C_5' & C_3'-H, J_o = 8.00 Hz), 7.10-7.08 (m, 1H, C_8-H), 5.39 (s, 2H, C_2-NH_2), 2.68 (s, 3H, C_{10}-CH_3), 2.47 (s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.3 (C_{6b}), 142.0 (C_2), 139.1 (C_{10a}), 138.7 (C_4), 131.4 (C_3), 131.2 (C_1'), 129.5 (C_{10a}), 128.7 (C_4'), 127.6 (C_5' & C_3'), 127.2 (C_6' & C_2'), 125.5 (C_{10}), 123.7 (C_8), 121.9 (C_9), 121.3 (C_5), 120.7 (C_6), 120.5 (C_{4a}), 119.5 (C_7), 118.7 (CN), 118.1 (C_{11b}), 117.2 (C_{6a}), 85.7 (C_1), 21.4 (C_4'-CH_3), 16.6 (C_{10}-CH_3); Anal. calcd. for $C_{25}H_{18}N_4O_2$: C, 73.88; H, 4.46; N, 13.78; Found: C, 73.97; H, 4.41; N, 13.86 %.

2-Amino-8-chloro-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8g**). Orange solid; yield: 259 mg (61%); m.p. 274-276°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3401 (NH_2 & indole NH), 2204 (CN), 1537 (asym NO_2), 1355 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.96 (br s, 1H, N_{11}-H), 8.04 (s, 1H, C_7-H), 7.87 (d, 1H, C_6-H, J_o = 9.20 Hz), 7.57 (d, 1H, C_5-

H, J_o = 8.80 Hz), 7.47 (d d, 2H, C_6' & C_2'-H, J_m = 2.00 Hz & J_o = 8.80 Hz), 7.34 (d, 2H, C_5' & C_3'-H, J_o = 8.00 Hz), 7.32-7.27 (m, 1H, C_9-H), 7.24-7.23 (m,1H, C_{10}-H), 5.43 (s, 2H, C_2-NH_2), 2.46 (s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.2 (C_2), 139.2 (C_{10a}), 137.4 (C_{11a}), 132.0 (C_4), 131.0 (C_1'), 129.3 (C_3), 128.9 (C_4'), 127.8 (C_{6b}), 127.2 (C_5' & C_3'), 126.2 (C_6'), 125.6 (C_2'), 124.3 (C_8), 123.4 (C_9), 122.6 (C_7), 121.5 (C_5), 121.0 (C_{4a}), 120.0 (C_6), 119.4 (C_{11b}), 119.1 (CN), 118.4 (C_{10}), 113.0 (C_{6a}), 112.8 (C_1), 21.3 (CH_3); Anal. calcd. for $C_{24}H_{15}ClN_4O_2$: C, 67.53; H, 3.54; N, 13.13; Found: C, 67.61; H, 3.50; N, 13.19 %.

2-Amino-3-nitro-4-(4'-methylphenyl)-11*H*-benzo[*a*]carbazol-1-carbonitrile (**8h**). Orange solid; yield: 286 mg (73%); m.p. 287-289°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (asym NH_2), 3379 (sym NH_2 & indole NH), 2207 (CN), 1538 (asym NO_2), 1360 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.97 (br s, 1H, N_{11}-H), 8.10 (d, 1H, C_7-H, J_o = 7.60 Hz), 7.95 (d, 1H, C_6-H, J_o = 9.20 Hz), 7.65 (d, 1H, C_5-H, J_o = 8.80 Hz), 7.53 (t, 1H, C_9-H, J = 7.6 Hz), 7.34-7.32 (m, 4H, C_6', C_2', C_5' & C_3'-H), 7.28-7.26 (m, 2H, C_{10} & C_8-H), 5.44 (s, 2H, C_2-NH_2), 2.47 (s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.2 (C_2), 139.3 (C_{10a}), 139.0 (C_{11a}), 131.3 (C_4), 131.3 (C_3 & C_1'), 128.9 (C_5' & C_3'), 127.0 (C_6' & C_2'), 124.0 (C_{6b}), 123.5 (C_9 & C_7), 122.4 (C_5 & C_8), 120.7 (C_6 & C_{4a}), 120.6 (C_{11b}), 120.4 (C_{10}), 119.5 (CN), 118.6 (C_{6a}), 111.7 (C_1), 21.3 (C_4'-CH_3); Anal. calcd. for $C_{23}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28; Found: C, 73.37; H, 4.15; N, 14.21 %.

Synthesis of 2-amino-3-nitro-4-aryl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9**). 1-(Dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol) and nitrostyrene **5** (1.0 mmol) in presence of morpholine (0.2 mL) and ethanol (20 mL) were intimately mixed in around bottom flask and the resulting mixture was refluxed for 6 hrs. The reaction was monitored by TLC, after completion of reaction the crude was poured into ice-water. The solid that separated out was filtered, washed with water and purified over column chromatography using petroleum ether: ethyl acetate (94:6) as eluent to afford the pure product **9**.

2-Amino-8-methyl-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9a**). Red solid; yield: 354 mg (90%); m.p. 295-297°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (asym NH_2), 3385 (sym NH_2 & indole NH), 2207 (CN), 1547 (asym NO_2), 1325 (sym NO_2); ^{1}H NMR (400

MHz, $CDCl_3$) (ppm) δ_H: 9.25 (br s, 1H, N_{11}-H), 7.46-7.41 (m, 3H, C_5', C_3' & C_4'-H), 7.36-7.34 (m, 2H, C_7 & C_{10}-H), 7.21 (d d, 2H, C_6' & C_2'-H, J_m = 1.40 Hz & J_o = 7.80 Hz), 7.15 (d, 1H, C_9-H, J_o = 8.80 Hz), 5.71 (s, 2H, C_2-NH_2), 2.83-2.79 (m, 2H, C_5-2H), 2.61-2.57 (m, 2H, C_6-2H), 2.44 (s, 3H, C_8-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 143.0 (C_{11b}), 141.4 (C_2), 136.4 (C_1'), 136.3 (C_3), 136.0 (C_4 & C_{10a}), 130.1 (C_5' & C_3'), 128.9 (C_{4a}), 128.6 (C_8), 128.2 (C_6' & C_2'), 127.9 (C_4'), 127.4 (C_{6b}), 125.6 (C_{11a}), 125.4 (C_9), 120.5 (C_7), 119.2 (CN), 118.1 (C_{6a}), 111.7 (C_{10}), 89.8 (C_1), 26.2 (C_5), 21.3 (C_6), 19.4 (CH_3); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{18}N_4O_2$: 394.1426; Found:394.1392; Anal. calcd. for $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 14.20; Found: C, 73.15; H, 4.56; N, 14.27 %.

2-Amino-10-methyl-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9b**). Red solid; yield: 338 mg (86%); m.p. 296-298°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3453 (asym NH_2), 3379 (sym NH_2 & indole NH), 2210 (CN), 1543 (asym NO_2), 1327 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.33 (br s, 1H, N_{11}-H), 7.45-7.40 (m, 4H, C_6', C_5', C_2' & C_3'-H), 7.23-7.20 (m, 2H, C_4' & C_7-H), 7.13-7.05 (m, 2H, C_9 & C_8-H), 5.70 (s, 2H, C_2-NH_2), 2.85-2.81 (m, 2H, C_5-2H), 2.62-2.58 (m, 2H, C_6-2H), 2.56 (s, 3H, C_{10}-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 143.1 (C_{11b}), 141.6 (C_2), 136.7 (C_1'), 136.5 (C_3), 136.1 (C_4 & C_{10a}), 130.3 (C_5' & C_3'), 129.0 (C_{4a}), 128.5 (C_8), 128.4 (C_6' & C_2'), 127.7 (C_4'), 127.3 (C_{6b}), 125.5 (C_{11a}), 125.2 (C_9), 120.7 (C_7), 119.3 (CN), 118.2 (C_{6a}), 111.8 (C_{10}), 89.7 (C_1), 26.3 (C_5), 21.5 (C_6), 19.3 (CH_3); Anal. calcd. for $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 14.20; Found: C, 73.16; H, 4.55; N, 14.28 %.

2-Amino-8-chloro-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9c**). Red solid; yield: 327 mg (79%); m.p. 294-296°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3440 (asym NH_2), 3355 (sym NH_2 & indole NH), 2210 (CN), 1550 (asym NO_2), 1329 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.70 (br s, 1H, N_{11}-H), 7.41 (s, 1H, C_7-H), 7.36-7.29 (m, 4H, C_6', C_5', C_2' & C_3'-H), 7.13-7.09 (m, 3H, C_4', C_{10} & C_9-H), 5.74 (s, 2H, C_2-NH_2), 2.69-2.66 (m, 4H, C_5 & C_6-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.8 (C_{11b}), 135.9 (C_2), 135.3 (C_1'), 130.8 (C_{10a}), 130.1 (C_3), 129.0 (C_4), 128.7 (C_5'), 128.4 (C_3'), 127.9 (C_6'), 127.3 (C_2'), 126.4 (C_4'), 125.7 (C_{4a}), 123.7 (C_{6b}), 123.4 (C_8), 121.0 (C_{11a}), 120.0 (C_9), 119.9 (C_7), 119.1 (CN), 118.5 (C_{6a}), 113.1 (C_{10}), 112.9 (C_1), 29.6 (C_5), 19.3 (C_6); Anal. calcd. for $C_{23}H_{15}ClN_4O_2$: C, 66.59; H, 3.64; N, 13.51; Found: C, 66.51; H, 3.60; N, 13.48 %.

2-Amino-3-nitro-4-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9d**). Red solid; yield: 340 mg (80%); m.p. 292-294°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3460 (asym NH_2), 3374 (sym NH_2 & indole NH), 2206 (CN), 1549 (asym NO_2), 1328 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.34 (br s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 8.00 Hz), 7.47-7.41 (m, 4H, C_6', C_5', C_3' & C_2'-H), 7.34-7.29 (m, 1H, 1H, C_{10}-H), 7.22-7.20 (m, 2H, C_9 & C_8-H), 7.15 (t, 1H, C_4'-H, J = 7.20 Hz), 5.70 (s, 2H, C_2-NH_2), 2.86-2.82 (m, 2H, C_5-2H), 2.62-2.58 (m, 2H, C_6-2H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 143.0 (C_{11b}), 141.4 (C_2), 137.9 (C_1' & C_{10a}), 136.2 (C_3), 135.8 (C_4), 129.0 (C_6' & C_2'), 128.8 (C_{4a}), 128.6 (C_5' & C_3'), 128.2 (C_4'), 127.9 (C_{6b}), 125.5 (C_{11a}), 125.4 (C_9), 120.9 (C_8 & C_7), 120.7 (C_{6a}), 119.8 (CN), 118.1 (C_{10}), 112.0 (C_1), 26.2 (C_5), 19.4 (C_6); Anal. calcd. for $C_{23}H_{16}N_4O_2$: C, 72.62; H, 4.24; N, 14.73; Found: C, 72.53; H, 4.28; N, 14.67 %.

2-Amino-8-methyl-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9e**).Red solid; yield: 359 mg (88%); m.p. 290-292 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3451 (asym NH_2), 3389 (sym NH_2 & indole NH), 2209 (CN), 1549 (asym NO_2), 1316 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.24 (br s, 1H, N_{11}-H), 7.35 (d, 2H, C_6' & C_2'-H, J_o= 7.80 Hz), 7.26 (m, 3H, C_7, C_{10} & C_3'-H), 7.14 (d, 1H, C_5'-H, J_o = 9.60 Hz), 7.14 (d, 1H, C_9-H, J_o = 7.80 Hz), 5.64 (s, 2H, C_2-NH_2), 2.82-2.78 (m, 2H, C_5-2H), 2.63-2.54 (m, 2H, C_6-2H), 2.44 (s, 3H, C_8-CH_3), 2.41(s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.8 (C_{11b}), 141.4 (C_2), 138.1 (C_8), 137.6 (C_4), 135.8 (C_1'), 133.1 (C_{10a}), 129.3 (C_4'), 128.9 (C_5' & C_3'), 128.6 (C_{4a}), 127.8 (C_8), 125.7 (C_6' & C_2'), 125.5 (C_{6b}), 124.9 (C_{11a}), 121.3 (C_9), 121.1 (C_7), 120.9 (C_{6a}), 118.3 (CN), 117.4 (C_{10}), 89.7 (C_1), 26.2 (C_5), 21.3 (C_6), 19.6 (C_8-CH_3), 16.5 (C_4'-CH_3); Anal. calcd. for $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72; Found: C, 73.60; H, 4.90; N, 13.68 %.

2-Amino-10-methyl-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (9f). Red solid; yield: 342 mg (84%); m.p. 288-290°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (asym NH_2), 3389 (sym NH_2), 3295 (indole NH), 2208 (CN), 1548 (asym NO_2), 1323 (sym NO_2); ^1H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.31 (br s, 1H, N_{11}-H), 7.41 (d, 1H, C_9-H, J_o= 8.00 Hz), 7.33-7.31 (m, 1H, C_7-H), 7.27-7.24 (m, 2H, C_6' & C_2'), 7.12-7.05 (m, 3H, C_5', C_3' & C_8-H), 5.63 (s, 2H, C_2-NH_2), 2.84-2.80 (m, 2H, C_5-2H), 2.64-2.60 (m, 2H, C_6-2H), 2.56 (s, 3H, C_{10}-CH_3), 2.41(s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.7 (C_{11b}), 141.5 (C_2), 138.0 (C_8), 137.4 (C_4), 135.7 (C_1'), 133.3 (C_{10a}), 129.5 (C_4'), 129.1 (C_5' & C_3'), 128.4 (C_{4a}), 127.7

(C_8), 125.5 (C_6' & C_2'), 125.3 (C_{6b}), 124.7 (C_{11a}), 121.5 (C_9), 121.0 (C_7), 120.7 (C_{6a}), 118.4 (CN), 117.3 (C_{10}), 89.5 (C_1), 26.3 (C_5), 21.5 (C_6), 19.7 (C_{10}-CH_3), 16.7 (C_4'-CH_3); Anal. calcd. for $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72; Found: C, 73.59; H, 4.88; N, 13.69 %.

2-Amino-8-chloro-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9g**). Red solid; yield: 321 mg (75%); m.p. 286-288 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3447 (asym NH_2), 3371 (sym NH_2 & indole NH), 2207 (CN), 1549 (asym NO_2), 1327 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.36 (br s, 1H, N_{11}-H), 7.52 (s, 1H, C_7-H, J_m = 2.00 Hz), 7.38 (d, 1H, C_{10}-H, J_o = 8.80 Hz), 7.27-7.24 (m, 4H, C_6', C_2', C_5' & C_3'-H), 7.09 (d, 1H, C_9-H, J_o = 8.80 Hz), 5.59 (s, 2H, C_2-NH_2), 2.81-2.77 (m, 2H, C_5-2H), 2.64-2.60 (m, 2H, C_6-2H), 2.41(s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.7 (C_{11b}), 141.6 (C_2), 138.3 (C_{10a}), 136.1 (C_3), 135.1 (C_4), 134.8 (C_6'), 132.9 (C_3'), 130.2 (C_4' & C_2'), 129.4 (C_{4a}), 128.9 (C_{6b}), 127.8 (C_6' & C_5'), 126.4 (C_8), 125.7 (C_{11a}), 125.6 (C_9), 119.8 (C_7), 119.1(CN), 118.1 (C_{6a}), 113.1 (C_{10}), 90.1 (C_1), 26.1 (C_5), 21.3 (C_6), 19.3 (C_4'-CH_3); Anal. calcd. for $C_{24}H_{17}ClN_4O_2$: C, 67.21; H, 4.00; N, 13.06; Found: C, 67.30; H, 4.04; N, 13.00 %.

2-Amino-3-nitro-4-(4'-methylphenyl)-5,6-dihydro-11*H*-benzo[*a*]carbazol-1-carbonitrile (**9h**). Red solid; yield: 338 mg (86%); m.p. 286-288°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3423 (asym NH_2), 3362 (sym NH_2 & indole NH), 2205 (CN), 1545 (asym NO_2), 1319 (sym NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.34 (br s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 8.00 Hz), 7.46 (d, 1H, C_{10}-H, J_o = 8.00 Hz), 7.33-7.29 (m, 1H, C_8-H), 7.26-7.25 (m, 2H, C_5' & C_3'-H), 7.17-7.13 (m, 1H, C_7-H), 7.09 (d, 2H, C_6' & C_2'-H, J_o = 8.00 Hz), 5.61 (s, 2H, C_2-NH_2), 2.86-2.88 (m, 2H, C_5-2H), 2.65-2.61 (m, 2H, C_6-2H), 2.41(s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 142.8 (C_{11b}), 141.5 (C_2), 138.2 (C_{10a}), 137.9 (C_3), 135.7 (C_4), 134.3 (C_2'), 133.1 (C_4'), 129.3 (C_5' & C_3'), 128.9 (C_{4a}), 127.9 (C_6' & C_2'), 127.1 (C_{6b}), 125.6 (C_{11a}), 125.4 (C_9), 120.8 (C_8), 120.6 (C_7), 120.4 (CN), 119.8 (C_{6a}), 111.7 (C_{10}), 89.8 (C_1), 29.6 (C_5), 26.2 (C_6), 21.3 (C_4'-CH_3); Anal. calcd. for $C_{24}H_{18}N_4O_2$: C, 73.08; H, 4.60; N, 14.20; Found: C, 73.15; H, 4.64; N, 14.13 %.

Synthesis of 2-imino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**11**). A mixture of 1-(dicyanomethylene)-2,3,4,9-

tetrahydrocarbazole **4** (1.0 mmol), malononitrile **2** (1.0 mmol), acenaphthenequinone **10** (1.0 mmol) and triethylamine (0.1 mmol) in dry ethanol (15 mL) was magnetically stirred and the progress of the reaction was monitored by checking TLC time to time, the solid precipitate appeared slowly at the end of the reaction after 5 h. Then, the precipitate was just filtered and it was washed with dry ethanol (3 x 5 mL), and it was dried to give pure compound **11**.

2-Imino-8-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**11a**). Pale yellow solid; yield: 395 mg (83%); m.p. 234-236 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3451 (indole NH), 3294 (imino NH), 2210 (CN), 1722 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 11.37 (br s, 1H, N_{11}-H), 10.95 (br s, 1H, C_2-imino NH), 8.50 (d, 1H, C_4', J_o = 8.00 Hz), 8.28 (d, 1H, C_2'-H, J_o = 6.40 Hz), 8.19 (d, 1H, C_5'-H, J_o = 8.40 Hz), 7.99 (t, 1H, C_6'-H, J = 7.40 Hz), 7.72 (t, 1H, C_3'-H, J_o = 7.40 Hz), 7.54 (d, 1H, C_{10}-H, J_o = 8.40 Hz), 7.43 (d, 1H, C_7'-H, J_o = 6.40 Hz), 7.31 (s, 1H, C_7-H), 7.22 (d, 1H, C_9-H, J_o = 8.40 Hz), 3.95 (d, 1H, C_{4a}-H, J = 10.80 Hz), 2.91-2.86 (m, 2H, C_6-2H), 2.32 (s, 3H, C_8-CH_3), 1.46-1.43 (m, 1H, C_{5a}-H), 1.23-1.21 (m, 1H, C_{5b}-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 198.7 (C=O), 156.9 (C_{11b}), 150.2 (C_2), 142.9 (C_{7b}'), 140.7 (C_{11a}), 134.7 (C_{4a}'), 131.0 (C_{7a}'), 130.9 (C_{1a}'), 130.5 (C_5'), 129.9 (C_8), 129.6 (C_{10a}), 128.8 (C_4'), 128.5 (C_6'), 128.1 (C_3'), 125.9 (C_{6b}), 124.5 (C_2'), 124.2 (C_9), 122.7 (C_7'), 121.7 (C_7), 118.9 (CN & CN), 116.0 (CN), 111.4 (C_{6a}), 110.9 (C_{10}), 94.9 (C_1), 58.8 (C_4), 41.2 (C_{4a}), 26.8 (C_3), 21.0 (C_5), 18.0 (C_6), 16.6 (CH_3); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{31}H_{19}N_5O$: 477.1586; Found:477.1554; Anal. calcd. for $C_{31}H_{19}N_5O$: C, 77.97; H, 4.01; N, 14.67; Found: C, 77.89; H, 4.05; N, 14.61 %.

2-Imino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**11b**). Pale yellow solid; yield: 376 mg (79%); m.p. 235-237°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3452 (indole NH), 3249 (imino NH), 2208 (CN), 1720 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 11.46 (br s, 1H, N_{11}-H), 10.59 (br s, 1H, C_2-imino NH), 8.48 (d, 1H, C_4'-H, J_o = 7.60 Hz), 8.26 (d, 1H, C_2'-H, J_o = 6.80 Hz), 8.18 (d, 1H, C_5'-H, J_o= 8.00 Hz), 7.98 (t, 1H, C_6'-H, J = 7.20 Hz), 7.71 (t, 1H, C_3'-H, J_o = 7.20 Hz), 7.43 (d, 1H, C_7'-H, J_o = 6.80 Hz), 7.35 (d, 1H, C_7-H, J_o = 7.20 Hz), 7.17 (d, 1H, C_9-H, J_o = 5.60 Hz), 7.00 (d, 1H, C_8-H, J = 5.60 Hz), 3.95 (d, 1H, C_{4a}-H, J = 10.40 Hz), 2.90-2.80 (m, 2H, C_6-2H), 2.46 (s, 3H, C_{10}-CH_3), 1.47-1.43 (m, 1H, C_5-H), 1.24-1.21 (m, 1H, C_5-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 198.5 (C=O),

156.8 (C_{11b}), 150.5 (C_2), 142.7 (C_{7b}'), 140.5 (C_{11a}), 134.5 (C_{4a}'), 131.3 (C_{7a}'), 131.0 (C_{1a}'), 130.3 (C_5'), 130.0 (C_8), 129.4 (C_{10a}), 128.6 (C_4'), 128.3 (C_6'), 127.8 (C_3'), 126.0 (C_{6b}), 124.7 (C_2'), 124.3 (C_9), 122.5 (C_7'), 121.6 (C_7), 118.7 (CN & CN), 116.1 (CN), 111.3 (C_{6a}), 110.7 (C_{10}), 94.8 (C_1), 58.5 (C_4), 41.3 (C_{4a}), 26.7 (C_3), 21.3 (C_5), 18.2 (C_6), 16.5 (CH_3); Anal. calcd. for $C_{31}H_{19}N_5O$: C, 77.97; H, 4.01; N, 14.67; Found: C, 77.90; H, 4.04; N, 14.62 %.

2-Imino-8-chloro-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**11c**). Pale yellow solid; yield: 362 mg (73%); m.p. 230-232°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3381 (indole NH), 3281 (imino NH), 2222 (CN), 1723 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 11.53 (br s, 1H, N_{11}-H), 11.23 (br s, 1H, C_2-imino NH), 8.49 (d, 1H, C_2'-H, J_o = 8.00 Hz), 8.28 (d, 1H, C_4'-H, J_o = 8.00 Hz), 8.19 (d, 1H, C_5'-H, J_o = 8.00 Hz), 7.99 (t, 1H, C_6'-H, J = 8.00 Hz), 7.74-7.63 (m, 3H, C_7, C_3' & C_{10}-H), 7.43 (d, 1H, C_7'-H, J_o = 8.00 Hz), 7.36 (d, 1H, C_9-H, J_o = 7.20 Hz), 3.95 (d, 1H, C_{4a}-H, J = 10.00 Hz), 2.91-2.87 (m, 2H, C_6-2H), 1.45-1.42 (m, 1H, C_5-H), 1.24-1.21 (m, 1H, C_5-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 198.7 (C=O), 156.6 (C_{11b}), 150.0 (C_2), 142.9 (C_{8b}'), 139.3 (C_{11a}), 134.7 (C_{5a}'), 130.9 (C_{8a}'), 130.8 (C_{2a}'), 130.4 (C_{10a}), 129.9 (C_5'), 129.6 (C_6'), 129.1 (C_4'), 128.4 (C_8), 128.0 (C_7'), 126.7 (C_{6b}), 125.7 (C_7), 124.6 (C_8'), 124.2 (C_9), 120.4 (C_3'), 120.3 (CN), 115.9 (CN), 115.2 (CN), 111.3 (C_{10}), 110.8 (C_{6a}), 95.5 (C_1), 58.7 (C_2), 31.8 (C_{4a}), 26.6 (C_3), 23.4 (C_5), 20.9 (C_6); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{30}H_{16}ClN_5O$: 497.1041; Found: 497.1008; Anal. calcd. for $C_{30}H_{16}ClN_5O$: C, 72.36; H, 3.24; N, 14.06; Found: C, 72.45; H, 3.20; N, 14.12 %.

2-Imino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**11d**). Pale yellow solid; yield: 370 mg (80%); m.p. 237-239°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3437 indole NH), 3269 (imino NH), 2212 (CN), 1717 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 11.42 (br s, 1H, N_{11}-H), 11.05 (br s, 1H, C_2-imino NH), 8.48 (d, 1H, C_4'-H, J_o = 6.80 Hz), 8.25 (d, 1H, C_2'-H, J_o = 7.20 Hz), 8.18 (d, 1H, C_5'-H, J_o = 6.80 Hz), 7.98-7.96 (m, 1H, C_7-H), 7.71-7.63 (m, 2H, C_6' & C_3'-H), 7.53 (d, 1H, C_{10}-H, J_o = 6.40 Hz), 7.43-7.36 (m, 2H, C_9& C_8-H), 7.06-7.08 (m, 1H, C_7'-H), 3.96 (d, 1H, C_{4a}-H, J = 10.0 Hz), 2.87-2.81 (m, 2H, C_6-2H), 1.42-1.39 (m, 1H, C_5-H), 1.23-1.22 (m, 1H, C_5-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 203.5 (C=O), 161.6 (C_{11b}), 154.7 (C_2), 147.6 (C_{7b}'), 145.9 (C_{11a}), 139.5 (C_{4a}'), 135.7 (C_{7a}'), 135.6 (C_{10a}), 135.2 (C_1'), 135.0 (C_5'), 134.7 (C_4'), 134.3 (C_6'), 133.4 (C_{6b}), 133.3 (C_3'), 132.7 (C_9), 130.6

(C_2'), 128.9 (C_8), 126.0 (C_7'), 125.9 (C_7), 120.3 (CN & CN), 118.8 (CN), 116.1 (C_{6a}), 115.6 (C_{10}), 99.2 (C_1), 63.5 (C_4), 46.1 (C_{4a}), 36.5 (C_3), 31.5 (C_5), 25.8 (C_6); Anal. calcd. for $C_{30}H_{17}N_5O$: C, 77.74; H, 3.70; N, 15.11; Found: C, 77.83; H, 3.74; N, 15.04 %.

Synthesis of 2-amino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12**). A mixture of 1-(dicyanomethylene)-2,3,4,9-tetrahydrocarbazole **4** (1.0 mmol), malononitrile **2** (1.0 mmol), acenaphthenequinone **10** (1.0 mmol) and morpholine (0.1 mmol) in methanol (15 mL) was magnetically stirred at 0°C for 5 h. The progress of the reaction was monitored by TLC. After completion of the reaction crude was purified by column chromatography over silica gel to give the pure compound**12**.

2-Amino-8-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12a**). Yellow solid; yield: 252 mg (53%); m.p. 245-247°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3444 (asym NH_2), 3365 (sym NH_2), 2208 (CN), 1631 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.23 (br s, 1H, N_{11}-H), 8.06-8.00 (m, 2H, C_5' & C_3'-H), 7.67-7.61 (m, 2H, C_6' & C_4'-H), 7.54 (t, 1H, C_7'-H, J_o = 7.60 Hz), 7.44 (d, 1H, C_8'-H, J_o = 7.60 Hz), 7.34 (d, 1H, C_9-H, J_o = 8.40 Hz), 7.28 (s, 1H, C_7-H), 7.13 (d, 1H, C_{10}-H, J_o = 8.40 Hz), 5.17 (s, 2H, C_2-NH_2), 3.36 (s, 3H, C_8-CH_3), 2.84-2.79 (m, 1H, C_6-H), 2.68-2.64 (m, 1H, C_6-H), 2.53-2.48 (m, 2H, C_5-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 165.8 (C=O), 134.3 (C_2), 130.7 (C_{8b}'), 130.0 (C_{4a}), 128.9 (C_{5a}'), 128.5 (C_{2a}' & C_{8a}'), 128.2 (C_{11b}), 128.0 (C_5' & C_6'), 127.4 (C_{10a} & C_8), 126.5 (C_3' & C_4'), 126.1 (C_5' & C_8'), 125.8 (C_{6b} & C_{11a}), 125.5 (C_8 & C_7), 125.4 (C_{6a} & C_{10}), 119.9 (CN, CN & CN), 86.3 (C_1), 52.2 (C_4), 33.3 (C_3), 29.6 (C_5), 25.1 (C_6), 16.6 (CH_3); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{31}H_{19}N_5O$: 477.1586; Found:477.1554; Anal. calcd. for $C_{31}H_{19}N_5O$: C, 77.97; H, 4.01; N, 14.67; Found:C, 77.89; H, 4.05; N, 14.61%.

2-Amino-10-methyl-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12b**). Yellow solid; yield: 233 mg (49%); m.p. 243-245°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3440 (asym NH_2), 3367 (sym NH_2), 2209 (CN), 1629 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.31 (br s, 1H, N_{11}-H), 8.06-8.01 (m, 2H, C_5' & C_3'-H), 7.66 (d, 1H, C_6'-H, J_o= 7.60 Hz), 7.64-7.61 (m, 1H, C_7'-H), 8.56-7.52 (m, 1H, C_4'-H), 7.46 (d, 1H, C_7-H, J_o = 7.20 Hz), 7.36 (d, 1H, C_8'-H, J_o = 7.60 Hz), 7.10 (d, 1H, C_9-H, J_o = 7.2 Hz), 7.05 (t, 1H, C_8-H, J_o = 7.6

Hz), 5.18 (s, 2H, C_2-NH_2), 3.37 (s, 3H, C_{10}-CH_3), 2.87-2.79 (m, 1H, C_6-H), 2.70-2.26 (m, 1H, C_6-H), 2.53-2.47 (m, 1H, C_5-H), 2.33-2.30 (m, 1H, C_5-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 150.8 (C=O), 134.3 (C_2), 131.9 (C_{8b}'), 130.8 (C_{4a}), 130.5 (C_{10a}), 130.3 (C_{5a}), 130.0 (C_{11b}), 129.3 (C_{2a}' & C_{8a}'), 128.7 (C_5' & C_6'), 128.5 (C_3' & C_4'), 128.0 (C_{6b}), 127.4 (C_7'), 126.0 (C_9 & C_8), 125.4 (C_{11a}), 125.2 (C_{10}), 122.9 (C_7), 122.6 (C_8), 120.6 (C_{6a}), 119.8 (CN), 118.2 (CN & CN), 111.9 (C_1), 51.9 (C_4), 33.5 (C_3), 29.6 (C_5), 25.9 (C_6), 19.1 (CH_3); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{31}H_{19}N_5O$: 477.1586; Found:478.1682; Anal. calcd. for $C_{31}H_{19}N_5O$:C, 77.97; H, 4.01; N, 14.67; O, 3.35; Found: C, 77.90; H, 4.04; N, 14.60 %.

2-Amino-1'-oxo-5,6-dihydro-11*H*-spiro[acenaphthylene-8',4-benzo[*a*]carbazole]-1,3,3-tricarbonitrile (**12d**). Yellow solid; yield: 231 mg (50%); m.p. 246-248°C; FT-IR (KBr, cm^{-1}) ν_{max}: 3450 (asym NH_2), 3370 (sym NH_2), 2202 (CN), 1637 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 9.33 (br s, 1H, N_{11}-H), 8.06 (d, 1H, C_5'-H, J_o = 8.0 Hz), 8.02 (d, 1H, C_3'-H, J_o = 8.4 Hz), 7.67 (d, 1H, C_6'-H, J_o = 7.6 Hz), 7.63-7.61 (m, 1H, C_7'-H), 7.55 (d, 1H, C_7'-H, J_o = 8.00 Hz), 7.52-7.49 (m, 1H, C_4'-H), 7.45 (d, 2H, C_7 & C_{10}-H, J_o = 7.60 Hz), 7.29 (t, 1H, C_8-H, J_o = 7.60 Hz), 7.12 (t, 1H, C_9-H, J_o = 7.60 Hz), 5.20 (s, 2H, C_2-NH_2), 2.87-2.83 (m, 1H, C_6-H), 2.71-2.67 (m, 1H, C_6-H), 2.51-2.45 (m, 1H, C_5-H), 2.23-2.28 (m, 1H, C_5-H); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 169.5 (C=O), 150.9 (C_2), 147.8 (C_{8b}), 137.9 (C_{4a}), 135.7 (C_{5a}'), 134.2 (C_{8a}'), 133.8 (C_{11b}), 131.9 (C_{10a}), 130.3 (C_2'), 130.0 (C_6'), 129.0 (C_5'), 128.7 (C_7'), 127.4 (C_8'), 126.0 (C_{6b}), 125.5 (C_4'), 125.3 (C_9), 125.2 (C_3'), 121.0 (C_{11a}), 120.6 (C_9 & C_8), 119.8 (CN & CN), 118.2 (CN), 115.8 (C_{6a}), 87.6 (C_1), 111.9 (C_{10}), 51.9 (C_4), 29.6 (C_3), 25.9 (C_5), 19.1 (C_6); HRMS (ESI) m/z: $[M]^+$ calcd for $C_{30}H_{17}N_5O$: 463.1430; Found: 463.2021; Anal. calcd. for $C_{30}H_{17}N_5O$: C, 77.74; H, 3.70; N, 15.11; Found: C, 77.66; H, 3.74; N, 15.17 %.

ASSOCIATED CONTENT

Electronic Supplementary Information (ESI)

Crystallographic data for compounds **9b** and **9d** and copies of ^{1}H,^{13}C NMR and mass spectra for new compounds

X-ray crystallographic data for compounds **9b** and **9d** (CIF-PDF)

Author Information

Corresponding Author

Tel: +91-422-2422311. E-mail: prasad_125@yahoo.com

Notes

The authors declare no competing financial interest.

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